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EC Harmonization Programme for Air Quality Measurements:

The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 carried out in October 2007 in Essen

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY

Executive Summary

In October 2007 in Essen (DE), 13 AQUILA and 5 WHO-EURO laboratories met at intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, CO, NO, NO_2 and O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on current situation to European Commission and can be used by participants in their QA/QC.

In terms of criteria imposed by European Commission, 65% of results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties while another 32% of results had good measured values but the reported uncertainties were either too small (5%) or too big (27%).

The comparability of results among AQUILA participants is satisfactory for O_3, SO_2, CO and NO measurement method but not for NO_2 where further harmonization is needed.

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Abbreviations:

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas phase titration
IE	Intercomparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
LANUV	North Rhine-Westphalia State Agency for Nature, Environment and Consumer protection
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	the oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
WHO CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols:

symbol	*explanation*
E_n	E_n – number statistic (ISO 13528; [17])
X	Assigned/reference value (ISO 13528; [17])
u_X	The standard uncertainty of the assigned/reference value (ISO 13528; [17])
U_X	The expended uncertainty of the assigned/reference value (ISO 13528; [17])
x_i	the average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [18])
$x_{i,j}$	j-th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [18])
U_{xi}	The expended uncertainty of the participant's value
z'	z'-score statistic (ISO 13528; [17])
σ_p	the standard deviation for proficiency assessment (ISO 13528; [17])
x*	robust average (Annex C ISO 13528; [17])
s*	robust standard deviation (Annex C ISO 13528; [17])
α	converter efficiency (EN 14211; [8])
s_r	repeatability standard deviation (ISO 5725; [18])
s_R	reproducibility standard deviation (ISO 5725; [18])
r	repeatability limit (ISO 5725; [18])
R	reproducibility limit (ISO 5725; [18])

1. Introduction

The Framework Directive 96/62/EC [1] on Ambient Air Quality Assessment and Management sets up a framework for a harmonized air quality assessment in Europe. One important objective of this Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. The first "Daughter Directive" [2] deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter and lead. Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements. The second "Daughter Directive" [3], dealing with benzene and carbon monoxide (CO), the third one [4] dealing with ozone (O_3), and the fourth one [5], dealing with heavy metals and polycyclic aromatic hydrocarbons, establish target values, the DQOs and reference methods for the mentioned compounds as well.

The European Commission (EC) has supported the development and publication of reference measurement methods [6], [7], [8] and [9] as European standards. Appropriate calibration methods [10], [11] and [12] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Framework Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes intercomparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [13] [14], but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the EC/ JRC/IES/ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization. The following report deals with the IE that took place from the 8th to the 11th of October 2007 in Essen (DE) at the North Rhine-Westphalia State Agency for Nature, Environment and Consumer Protection (LANUV) in joint cooperation of EC/ JRC/IES/ERLAP, WHO CC and LANUV.

ERLAP has been organizing IEs since 1990 aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Nowadays the main objective, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [15], comprises a more systematic approach that offers alert mechanism for the purposes of the EC and is also useful to NRLs in quality assurance of their implemented quality systems. The methodology of organization of IEs was developed by ERLAP and is described in a position paper on the organization of intercomparison exercises for gaseous air pollutants [16]. This position paper is currently a proposal to the AQUILA and the final agreement of position paper is foreseen to take place during 2008. Then it will be applied throughout all future IEs.

The evaluation scheme applied to this IE is described in detail in the position paper [16] and it reflects the inputs given by AQUILA. Firstly, it was acknowledged that the evaluation scheme should have common criteria, to alert the EC on the possible performance failure, and not to base these alerts on claimed uncertainty of participants. For that purpose the common criterion was proposed to AQUILA and the z'-score method [17] was implemented in to the evaluation scheme. The common criterion is

derived from the uncertainty requirements for calibration gases stated in the European standards [6], [7], [8] and [9], which are consistent with the DQOs of European Directives. In view of AQUILA, NRLs with overall unsatisfactory results of the z'-score evaluation (one unsatisfactory or two questionable results per parameter) are required to repeat their participation to the next IE in order to demonstrate remediation measures [16]. Secondly, it was acknowledged that the evaluation scheme should be useful to participants accredited according to ISO 17025 and thus should include measurement uncertainty of participants. For that purpose, participants measurement results (measurement values and uncertainties) are compared to assigned values applying the E_n – number method [17].

Beside the proficiency of participating laboratories the repeatability and reproducibility of standardized measurement methods [18], [19] and [20] are evaluated as well. These group evaluations will be used in a separate communication as the indicators of trends of quality of measurements over different IEs undertaken by ERLAP.

2. Communication and time schedule

The IE was announced in February 2007 to the members of the AQUILA network and WHO CC representative. A registration letter was send to interested parties and the registration was closed in July 2007 with the full list of 18 participating laboratories. The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 8th October 2007, for the installation of their equipment. The calibration of NOx and O_3 analysers was carried out on Tuesday morning and the generation of NOx and O_3 gas mixtures started at 11:00. The calibration of SO_2 and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO_2 gas mixtures started at 20:00. The test gases generation finished on Thursday at 7:00 a.m..

3. Participants

The majority of participants were organizations dealing with the routine ambient air monitoring on the national or regional levels of EU member states. The national representatives came from Austria, Germany, Denmark, Spain, Finland, Hungary, Lithuania, Slovak Republic and The Netherlands, and regional representatives came from Flemish region (Belgium), Federal State of North Rhine-Westphalia (Germany) and Ile de France (France).

The participants which were invited by the WHO CC also consisted of organizations dealing with the routine ambient air monitoring at national level coming from Albania, Macedonia and Ukraine, and two institutes involved in health related studies from Albania and Belgrade (Serbia).

Table 1: The list of participating organizations.

Country	Name of Organization	IE code
Austria	Umweltbundesamt	A
Belgium	Flemish Environment Agency	B
Germany	Federal Environment Agency	C
Germany	Landesamt für Natur, Umwelt und Verbraucherschutz	D
Denmark	National Environmental Research Institute	E
Spain	Instituto de Salud Carlos III	F
Finland	Finnish Meteorological Institute	G
France	Airparif	H
Hungary	Environmental Protection & Water Management Research Institue	I
Lithuania	Lithuanian Environmental Protection Agency	J
Netherlands	National Institute for Public Health and the Environment	K
Slovak Republic	Slovak Hydrometeorological Institute	L
European Commission	European Reference Laboratory for Air Polution	M
Albania	Hydrometeorological Institute	N
Republic of Macedonia	Ministry of Environment and Physical Planning	O
Republic of Serbia	Institute for Public Health, Beograd	P
Ukraine	Marzeyev Inst. for Hygiene and Medical Ecology	
Albania	Institute of Public Health	

The team from Ukraine participated to the IE but has used instrumentation that is intended for measurements at concentrations higher than the IE testing range. Consequently, it didn't report results.

The team from the Institute of Public Health (Tirana, Albania) had problems with the transportation of their equipment and could not participate actively in measurements but has nevertheless attended the IE as an observer.

4. Preparation of test mixtures

The LANUV IE facility (FINCA) has been described in several reports [21] and [22]. During this IE, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around the European Air Quality limit values, critical levels and assessment thresholds.

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO_2 or CO using thermal mass flow controllers [12]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method [23] in the conditions of excess NO.

The participants were required to report three half-hour-mean measurements for each concentration level in order to evaluate the repeatabilities of standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurements were reported. In Table 2, the sequence program of generated test gases – 'target values' is given.

Table 2: The sequence program of generated test gases – target values
The steps that were removed from program or evaluation are stroked through.

day	start time	duration	operation or run number	zero air	NO	NO_2	O_3	CO	SO_2
		(h)		(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(µmol/mol)	(nmol/mol)
08-Oct	12:00	6	installation						
09-Oct	08:00	3	calibration						
09-Oct	11:00	1	NO & NO_2 & O_3 run 0	0					
09-Oct	12:00	2	NO & NO_2 run 1		500	0			
09-Oct	14:00	2+2	NO & NO_2 run 2		~~380~~	120			
09-Oct	18:00	2	O_3 run 1				120		
09-Oct	20:00	2	NO & NO_2 run 3		250	0			
09-Oct	22:00	2	NO & NO_2 run 4		146	104			
09-Oct	00:00	2	O_3 run 2				104		
10-Oct	02:00	2	NO & NO_2 run 5		150	0			
10-Oct	04:00	2	NO & NO_2 run 6		90	60			
10-Oct	06:00	2	O_3 run 3				60		
10-Oct	08:00	2	NO & NO_2 run 7		50	0			
10-Oct	10:00	2	NO & NO_2 run 8		29.1	20.9			
10-Oct			~~O_3 run 4~~				~~20.9~~		
10-Oct	12:00	2	NO & NO_2 run 9		15.7	0			
10-Oct	14:00	2	NO & NO_2 run 10		2.1	13.6			
10-Oct	16:00	2	O_3 run 5				13.6		
10-Oct	< 18:00	2	calibration						
10-Oct	20:00	1	CO & SO_2 run 0	0					
10-Oct	21:00	2:30	CO & SO_2 run 1					8.6	132
10-Oct	23:30	2	CO & SO_2 run 2					6	47
11-Oct	01:30	2	CO & SO_2 run 3					4.3	18.8
11-Oct	03:30	2	CO & SO_2 run 4					2	7.5
11-Oct	05:30	2	CO & SO_2 run 5					1	3
11-Oct	07:30	1		0					

Some difficulties with the test gas generation arose during the realization of test gas sequence and the second NO_X run (see Table 2) was prolonged for two more hours then expected. Also evident irregularities in the stability of NO measurements were observed by all participants during this run. This issue was discussed between the organizers and the participants at the final meeting of IE and the participants were instructed to report the last three half-hour-mean measurements. The lack of stability

suggested that the NO homogeneity over the whole testing bench was also questionable. Consequently, this run was removed from further evaluation concerning NO.

The fourth O_3 run (see Table 2) had to be overstepped, due to the delay of second NO_X run, to kip up with the schedule. None of these two changes in test gas sequence have jeopardized the objectives of the IE.

5. Evaluation of laboratory's measurement proficiency

To evaluate participants measurement proficiency the methodology described in ISO 13528 [17] was applied. It has been agreed among the members of the AQUILA to take the measurement results of ERLAP as the assigned/reference values for the whole IE [16]. The traceability of ERLAPs measurement results and the method applied to validate them are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAPs measurement results.

All data reported by participating laboratories are presented in Annex B.

As it is described in the position paper [16], the proficiency of participant's was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests if the difference between the participants measured value and assigned/reference value remains within the limits of common criterion, while the second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of criterion, that is calculated individually for each participant, from the uncertainty of participants measurement result and the uncertainty of assigned/reference value.

z' - score

The z'- score statistic is calculated according to ISO 13528 [17] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \qquad (1)$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_X' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 3.

In the European standards [6], [7], [8] and [9] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to verify the accuracy of above mentioned 'zero gas' and calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [17] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2,5 % at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IEs [24]. The linear function parameters of σ_p are given in Table 3.

Table 3: The standard deviation for proficiency assessment as a linear function of concentration (c) with linear function parameters: slope (a) and intercept (b).

	$\sigma_p = a \cdot c + b$	
	a	b
		nmol/mol
SO2	0.024	0.4
CO	0.023	100
O3	0.022	0.5
NO	0.025	0.35
NO2	0.023	0.46

During November 2008 AQUILA meeting, σ_p was enlarged, to 1 ppb at zero concentration of SO_2, O_3, NO, NO_2, and approved. It has been agreed that this change is noted in all relevant and not yet published IE reports and applied to all future IEs.

The z'-score evaluation allows the following criteria to be used for the assessment of results:

- $|z'| \leq 2$ are designated satisfactory.
- $2 < |z'| \leq 3$ are designated questionable.
- $|z'| > 3$ are designated unsatisfactory. Scores falling in this range are very unusual and are taken to indicate that the cause of the event should be investigated and remedied.

The results of z'-score evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as z' = ±2 and z' = ±3 lines.

Figure 1: The z'-score evaluations of SO_2 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (3 nmol/mol), 4 (7 nmol/mol), 3 (19 nmol/mol), 2 (47 nmol/mol), 1 (132 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

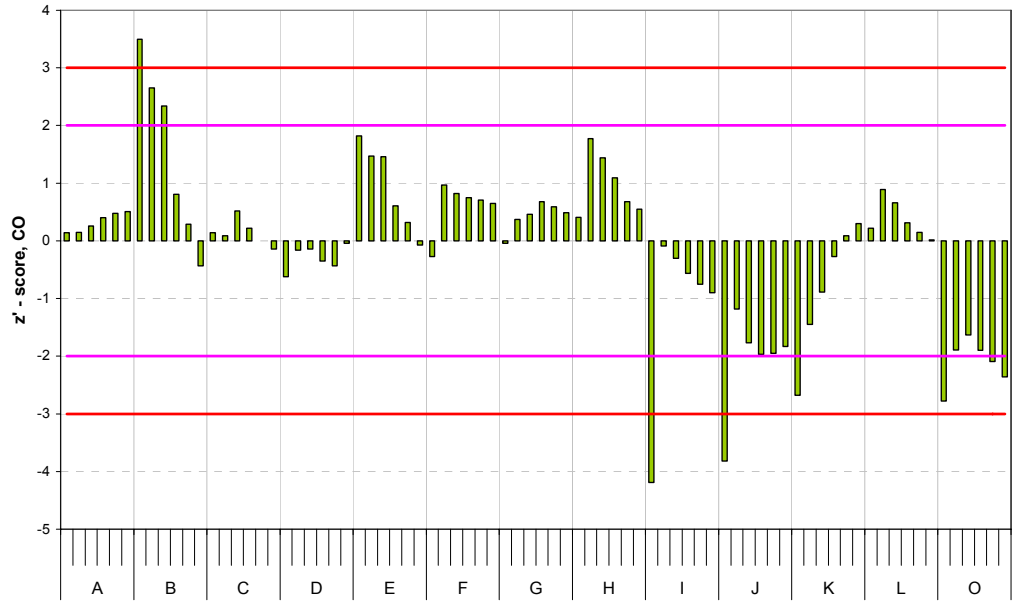

Figure 2: The z'-score evaluations of CO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 µmol/mol), 5 (1 µmol/mol), 4 (2 µmol/mol), 3 (4 µmol/mol), 2 (6 µmol/mol), 1 (9 µmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

Figure 3: The z'-score evaluations of O_3 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (14 nmol/mol), (run 4 not given see chapter 4), 3 (60 nmol/mol), 2 (104 nmol/mol), 1 (120 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

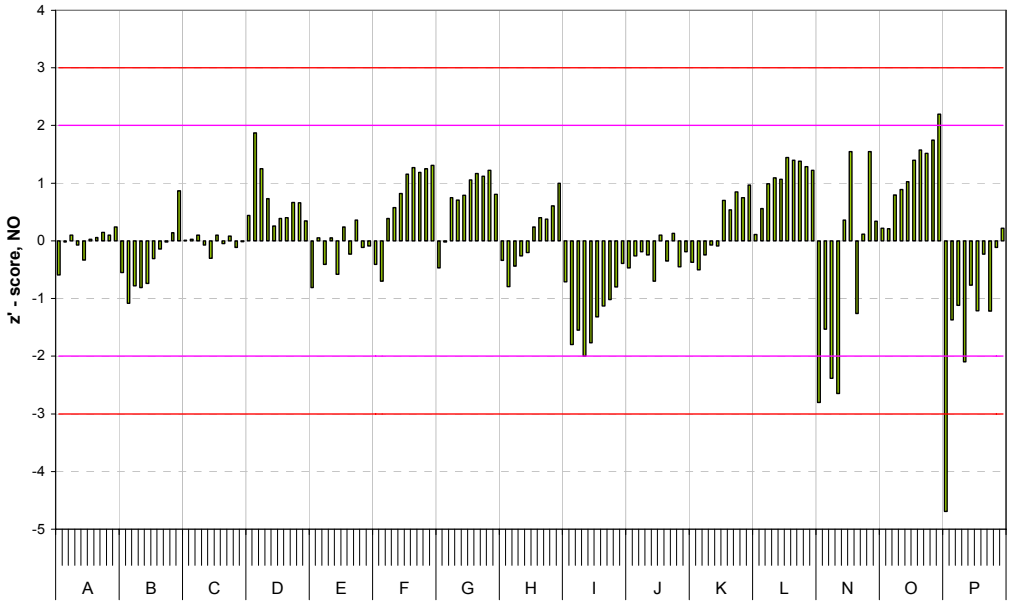

Figure 4: The z'-score evaluations of NO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , (run 2 not given see chapter 4), 1 (500 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

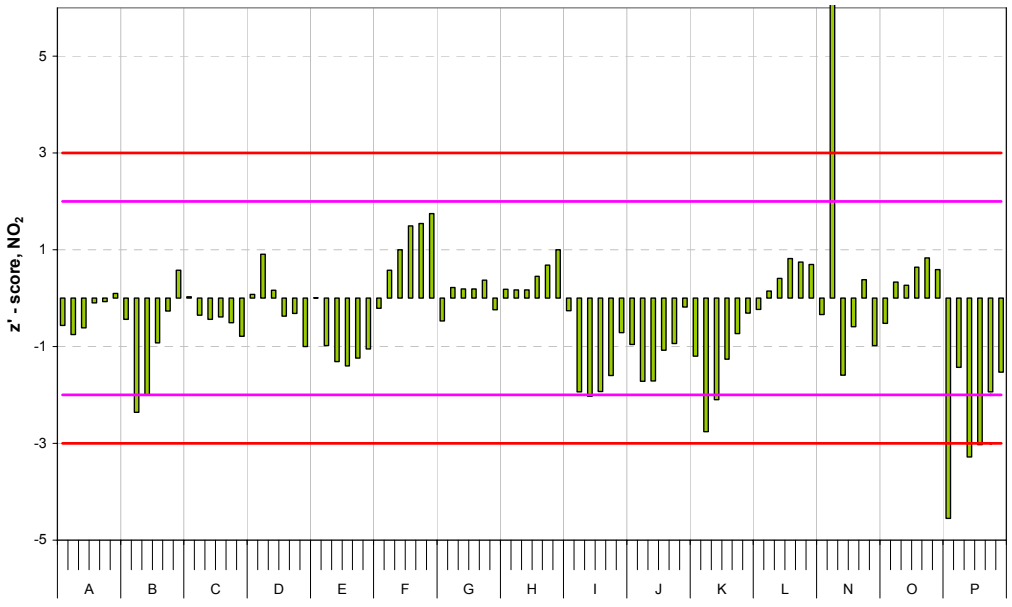

Figure 5: The z'-score evaluations of NO_2 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (14 nmol/mol), 8 (21 nmol/mol), 6 (60 nmol/mol), 4 (104 nmol/mol), 2 (120 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

E_n - number

The normalised deviations [17] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \qquad (2)$$

where 'X' is the assigned/reference value with expanded uncertainty 'U_X' and 'x_i' is the participant's average value with expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

In Figure 6 to Figure 10 the biases of each participant (xi-X) are plotted and error bars are used to denote the value of denominator of equation 2 $\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 3) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

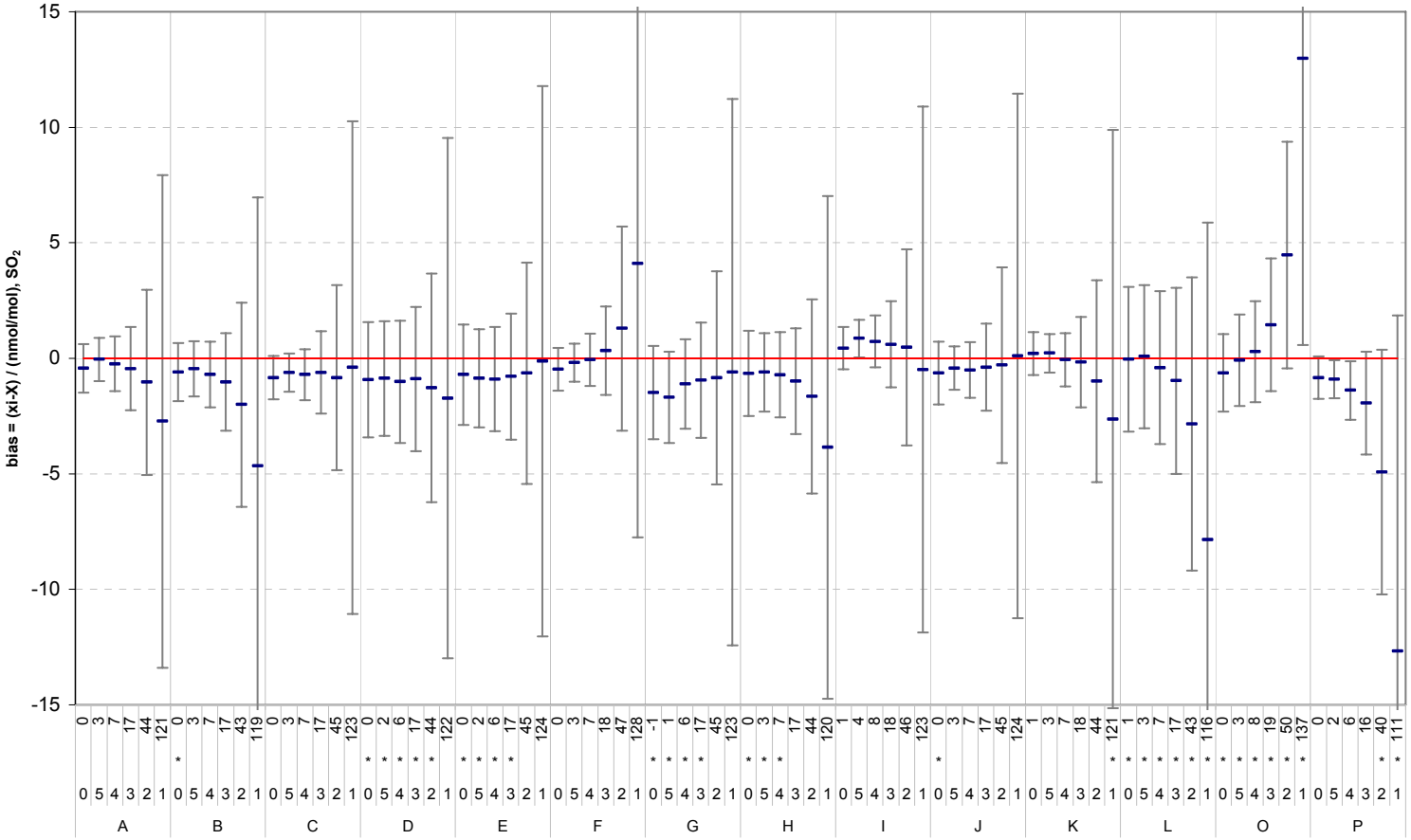

Figure 6: Bias of participant's SO_2 measurement results
together with the uncertainty of bias presented with error bar are given for each tested concentration level. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

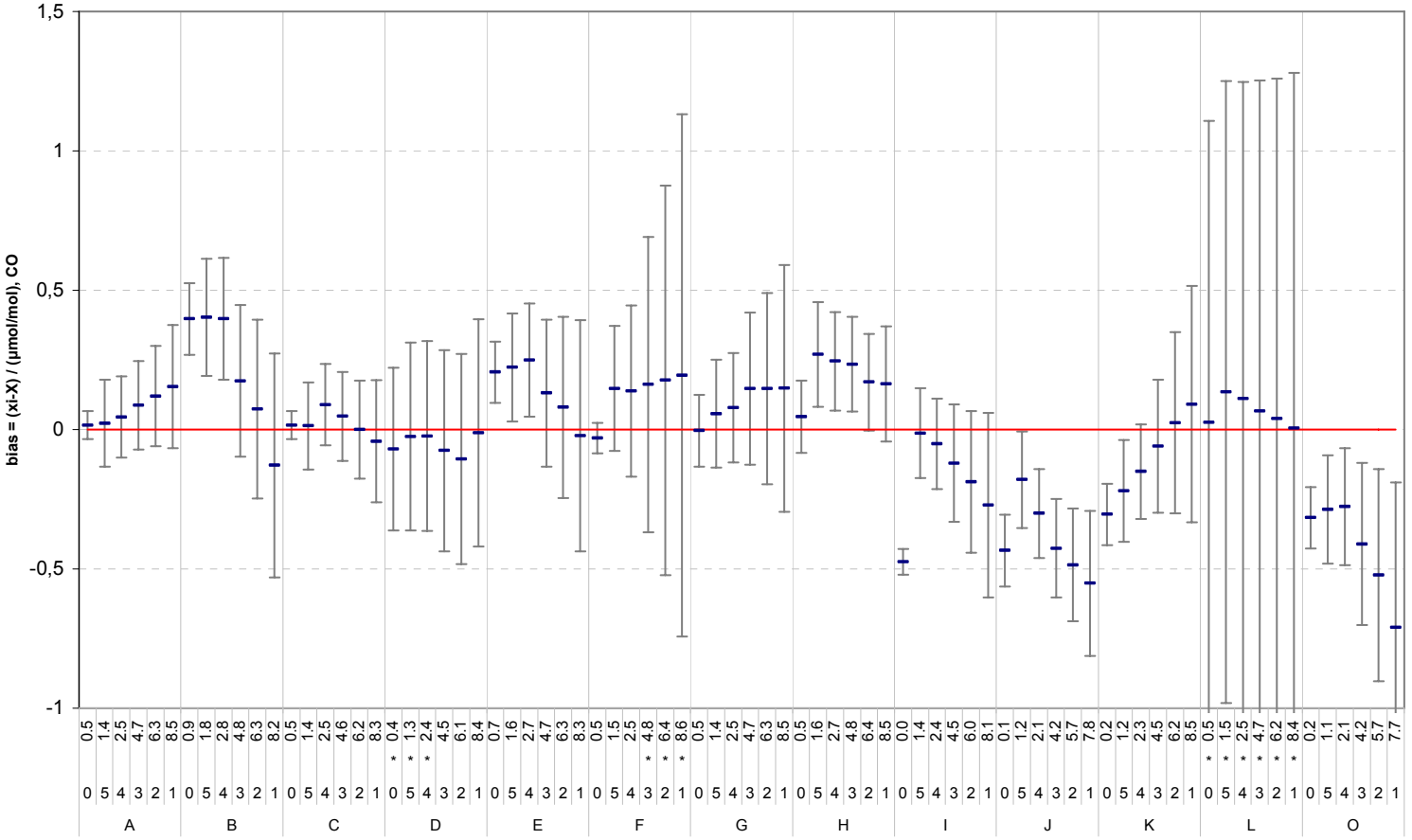

Figure 7: Bias of participant's CO measurement results
together with the uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

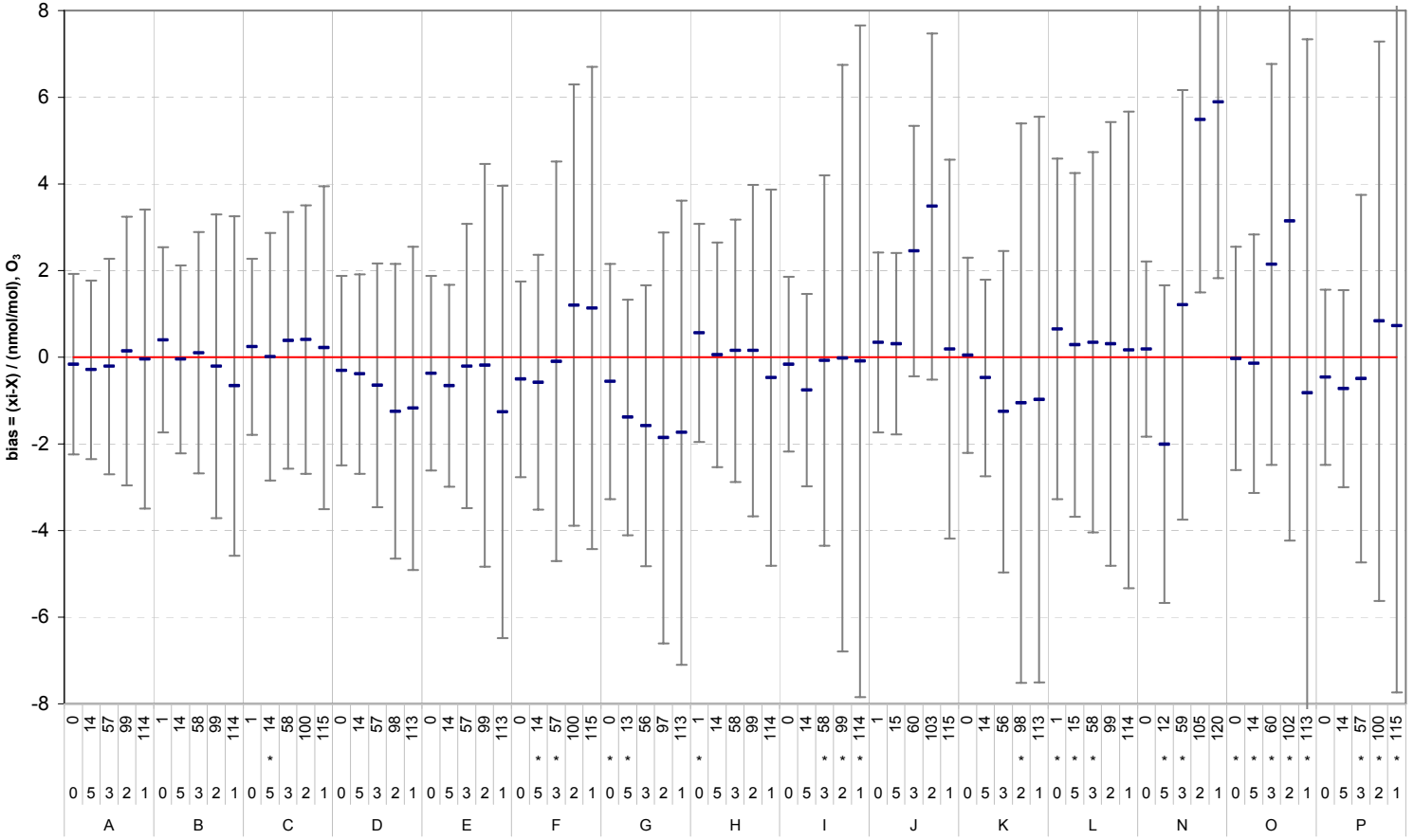

Figure 8: Bias of participant's O_3 measurement results
together with the uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

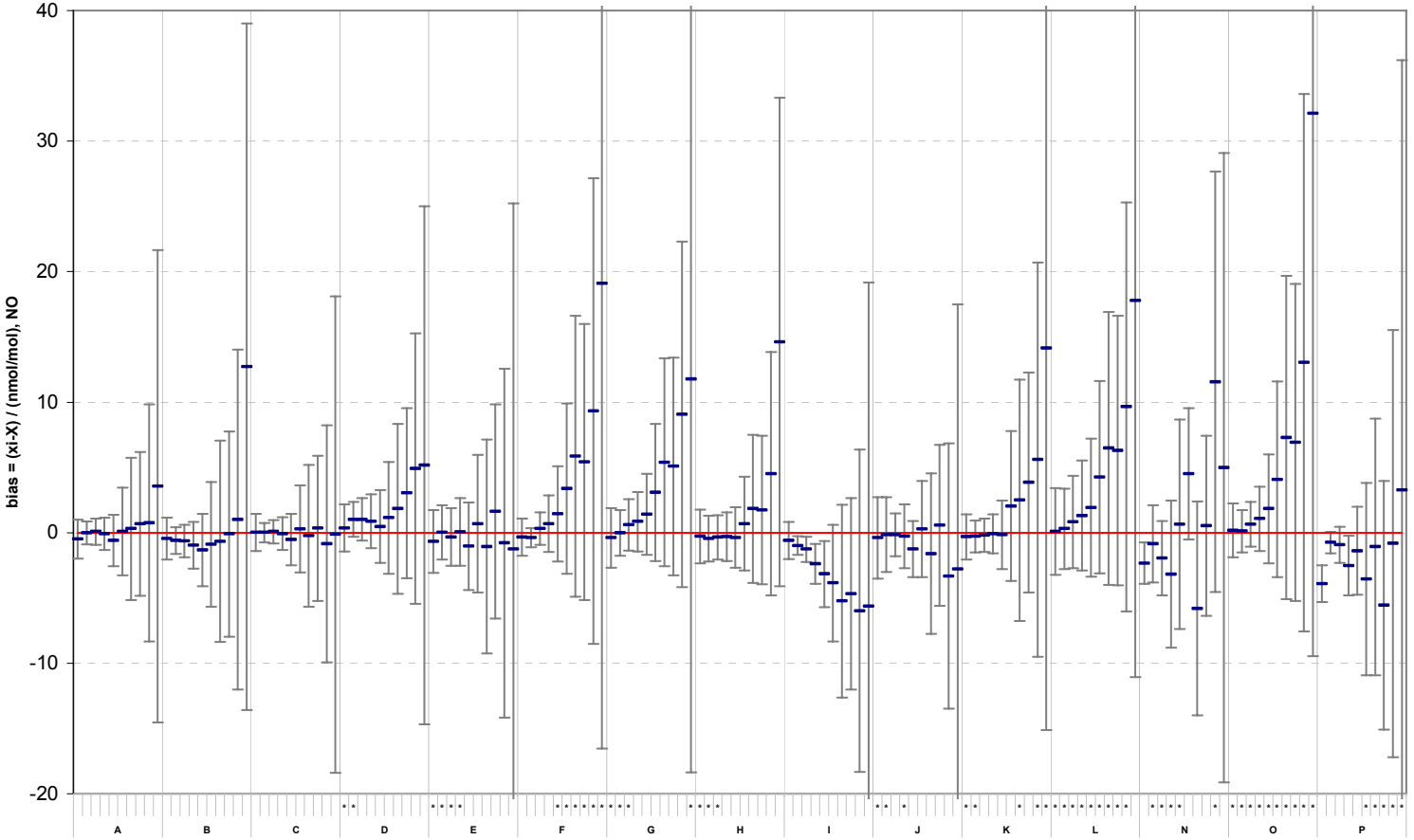

Figure 9: Bias of participant's NO measurement results
together with the uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. Evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , (run 2 not given see chapter 4), 1 (500 nmol/mol)). The '*' mark indicates reported standard uncertainties bigger then σ_p.

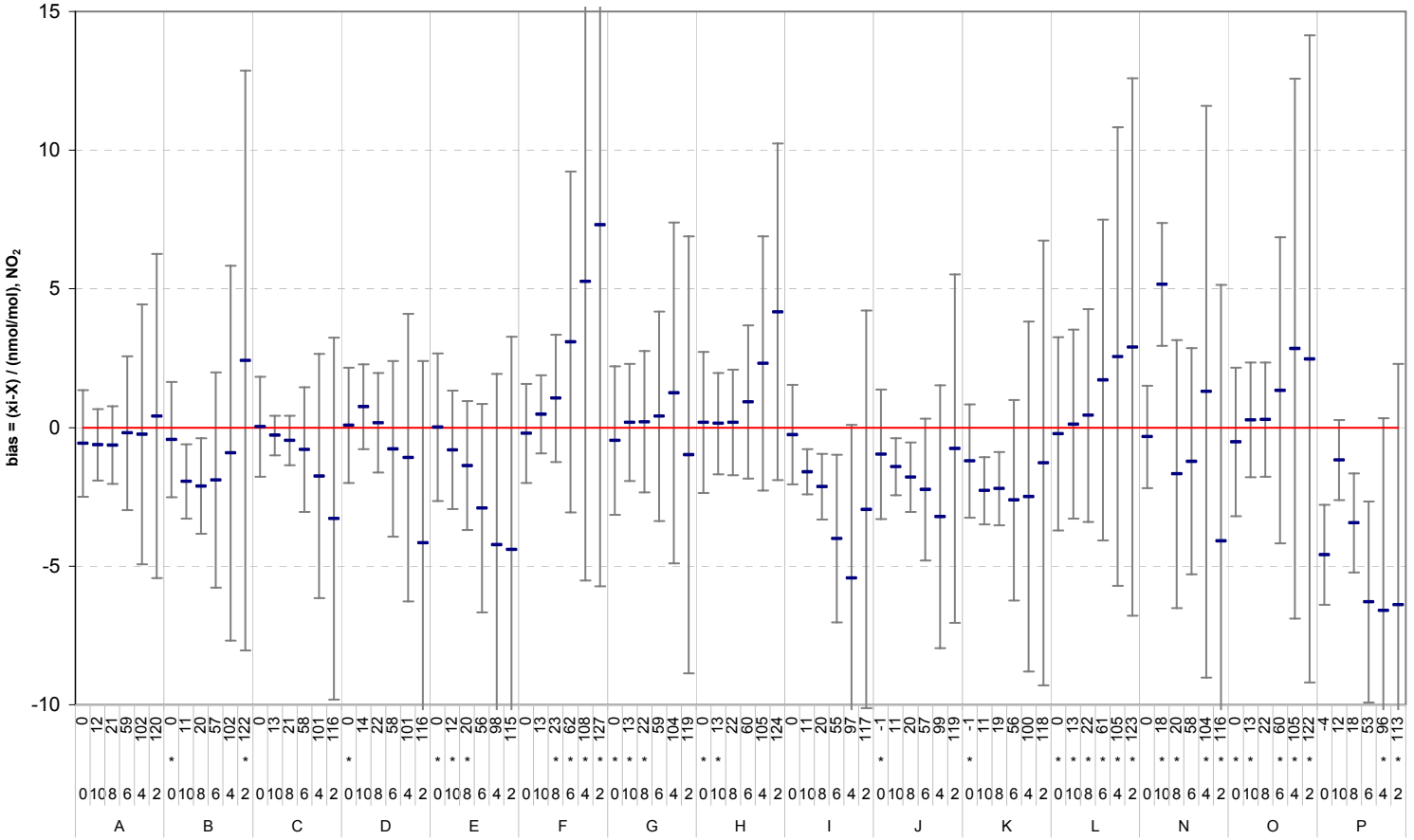

Figure 10: Bias of participant's NO_2 measurement results
together with the uncertainty of bias presented with error bar are given for tested concentration level with NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 2). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6-Figure 10). Since the results of NO_2 runs 1,3,5,7 and 9 were not treated in proficiency evaluation the biases of these runes are presented in Figure 11.

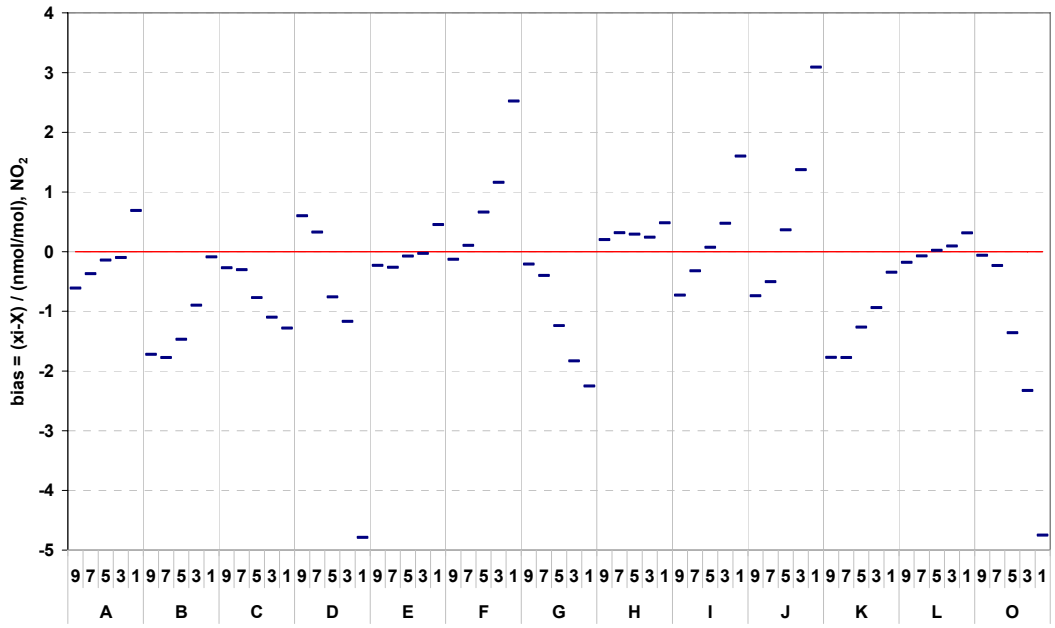

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
At these test gas mixtures the concentration levels of NO_2 were zero and the concentration levels of NO were not zero (see Table 2). In that perspective the figure shows the effect of NO concentration on NO_2 measurements.

The efficiency of NO_2-to-NO converters of NO_X analyzers

Since NO and NO_2 test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participants NO and NO_2 measurements before and after oxidation by O_3. The converter efficiency (α) is calculated using equation 3 [8]:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad (3)$$

The O_3 measurements of each participant can also be compared to NO_2 measurements by calculating Δ using equation 4:

$$\Delta = [O3]_{i+1} - ([NO2]_i - [NO2]_{i-1}) \qquad (4)$$

Ideal values for α and Δ are 100% and 0 nmol/mol respectively.

The first GPT test (at 120 ppb of NO_2) was jeopardised and discarded, because of the insufficient reproducibility of NO_X generation. The evaluation of equation 4 can not be made for the forth GPT test (at 22 ppb NO_2), due to cancellation of O_3 run 4 (see chapter 4), and fifth GPT test (at 14 ppb of NO_2), because O_3 was not completely reduced duo to insufficient excess of NO. The remaining evaluations of equations 3 and 4 for each participant at different concentration levels are given in Table 4.

Table 4: The efficiency of NO_2-to-NO converters.

IE code	NO_2 nmol/mol	α %	Δ (nmol/mol) nmol/mol
A	14	100.6	
A	22	101.1	
A	60	100.1	-0.3
A	100	100.5	-0.9
B	14	99.9	
B	22	100.0	
B	60	99.4	0.4
B	100	99.6	-1.4
C	14	100.8	
C	22	101.3	
C	60	101.5	0.3
C	100	101.3	-0.1
D	14	102.8	
D	22	101.1	
D	60	99.4	-0.8
D	100	98.9	-2.5
E	14	99.7	
E	22	99.8	
E	60	98.7	2.5
E	100	98.9	2.8
F	14	100.6	
F	22	100.8	
F	60	100.5	-2.7
F	100	100.9	-4.1
G	14	99.5	
G	22	100.1	
G	60	99.4	-3.4
G	100	99.8	-6.1

IE code	NO_2 nmol/mol	α %	Δ (nmol/mol) nmol/mol
H	14	100.3	
H	22	99.5	
H	60	99.7	-0.6
H	100	100.0	-3.1
I	14	96.4	
I	22	94.7	
I	60	95.8	3.8
I	100	96.1	4.7
J	14	95.8	
J	22	98.3	
J	60	99.3	4.9
J	100	100.0	6.9
K	14	96.6	
K	22	98.1	
K	60	97.5	-0.1
K	100	97.5	-0.7
L	14	99.7	
L	22	99.4	
L	60	99.7	-1.5
L	100	99.9	-3.4
M	14	101.5	
M	22	99.9	
M	60	100.6	-0.2
M	100	100.7	-1.2
O	14	99.8	
O	22	98.8	
O	60	99.7	-0.7
O	100	99.8	-3.2

Uncertainty of converter efficiency evaluation at higher NO_2 concentration is in general smaller then at lower NO_2 concentration. By taking standard deviations of repeatable measurements of quantities in equation 3 the standard uncertainty of converter efficiency averaged over all participants is evaluated to approximately 1% (at 100 nmol/mol of NO_2) and 2% (at 14 nmol/mol of NO_2).

7. Discussion

For the general assessment of quality of each result the decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score good and En-number ok) but reported uncertainty is to big
- a3: measured value is satisfactory (z'-score good) but reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to large reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is bad (z'-score bad) but due to large reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is bad (z'-score bad and En-number not ok)

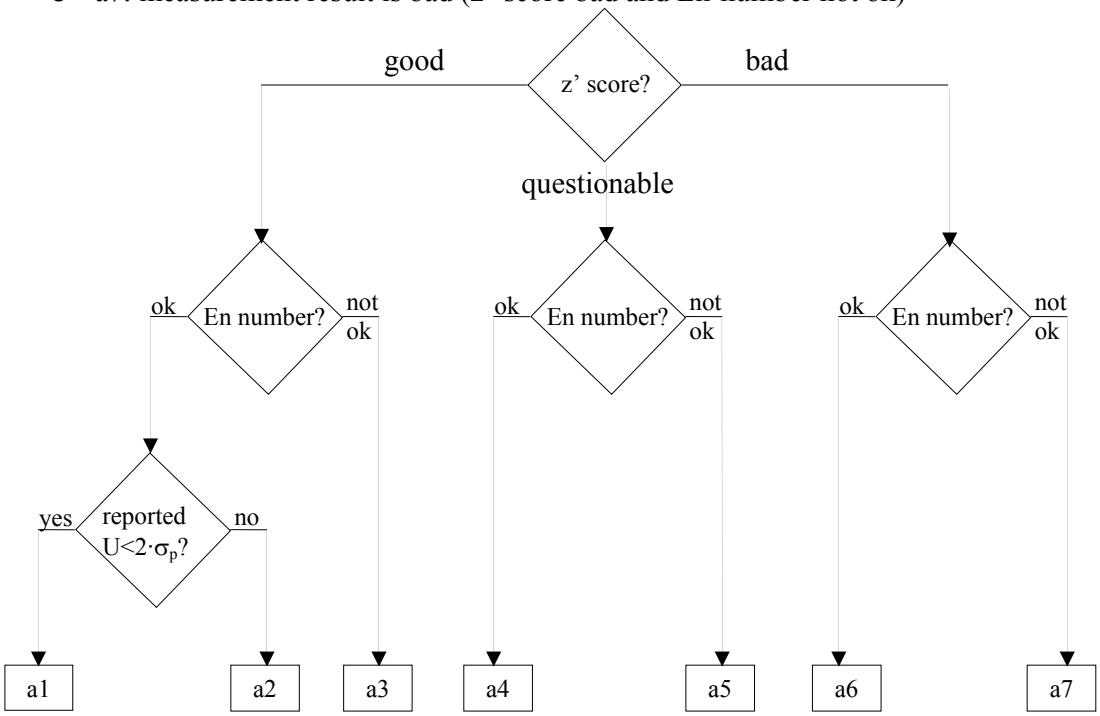

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in Table 5. For clarity reasons, notation 'a1' is not inserted in Table 5 and all empty spaces represent 'a1' results.

Table 5: The general assessment of proficiency results.
Empty spaces represent 'a1' results while results not reported are represented by 'nv' (no value).

	run number	conc. level	IE code														
			A	B	C	D	E	F	G	H	I	J	K	L	N	O	P
SO_2 (nmol/mol)	0	1		a2		a2	a2		a4	a2		a2		a2	nv	a2	
	5	3				a2	a2		a4	a2	a3			a2	nv	a2	a3
	4	7				a2	a2		a2	a2				a2	nv	a2	a3
	3	18				a2	a2		a2					a2	nv	a2	
	2	45				a2								a2	nv	a2	a4
	1	124											a2	a2	nv	a4	a4
CO (µmol/mol)	0	0,5		a7		a2	a3				a7	a7	a5	a2	nv	a5	nv
	5	1,4		a5		a2	a3			a3			a3	a2	nv	a3	nv
	4	2,4		a5		a2	a3			a3		a3		a2	nv	a3	nv
	3	4,6						a2		a3		a3		a2	nv	a3	nv
	2	6,2						a2				a3		a2	nv	a5	nv
	1	8,4						a2				a3		a2	nv	a5	nv
O_3 (nmol/mol	0	0							a2	a2				a2		a2	
	5	14			a2			a2	a2					a2	a2	a2	
	3	58						a2			a2			a2	a2	a2	a2
	2	99									a2		a2		a3	a2	a2
	1	114									a2				a3	a2	a2
NO (nmol/mol)	0	4				a2	a2		a2	a2		a2	a2	a2	a5	a2	a7
	10	3				a2	a2		a2	a2	a3	a2	a2	a2	a2	a2	
	9	15					a2		a2	a2	a3			a2	a4	a2	
	8	28					a2				a5	a2		a2	a4	a2	a5
	7	49						a2			a3			a2	a2	a2	
	6	88						a2						a2		a2	a2
	5	146						a2					a2	a2		a2	a2
	4	142						a2						a2		a2	a2
	3	242						a2					a2	a2	a2	a2	a2
	1	484						a2	a2				a2			a4	a2
NO_2 (nmol/mol)	0	0		a2		a2	a2		a2	a2		a2	a2	a2		a2	a7
	10	13		a5			a2		a2	a2	a3	a3	a5	a2	a7	a2	
	8	22		a5			a2	a2	a2		a5	a3	a5	a2	a2		a7
	6	59						a2			a3			a2		a2	a7
	4	102						a2						a2	a2	a2	a2
	2	120		a2				a2						a2	a2	a2	a2

Laboratory B had unsatisfactory results at the low concentration levels of CO. Unsatisfactory were also results at two NO_2 concentration levels, which could be due to large effect of NO on NO_2 measurements (Figure 11).

Laboratory E had underestimated uncertainty at low concentration levels of CO.

Laboratory G had unsatisfactory results at the low concentration levels of SO_2.

Laboratory H had underestimated uncertainty at low concentration levels of CO.

Laboratory I had unsatisfactory results at the zero concentration level of CO and one NO and NO_2 concentration level. Also converter efficiency was not good (Table 4).

Laboratory J had unsatisfactory results at the zero concentration level of CO and underestimated uncertainty for four CO and two NO concentration levels.

Laboratory K had unsatisfactory result at zero concentration level of CO. It was revealed through exchange of information after the IE that laboratory K has used the gas in the testing bench as zero air in their CO calibration. Unsatisfactory were also results at two NO_2 concentration levels, which could be due to large effect of NO on NO_2 measurements (Figure 11) and also not optimal converter efficiency (Table 4).

Laboratory N had underestimated uncertainty for two O3 and two NO concentration levels. Unsatisfactory were also results at low NO concentration levels and one NO_2 concentration level.

Laboratory O had unsatisfactory results for all concentration levels of CO. Since it didn't use travelling standards for checks/calibration during IE it is hard to investigate the cause of large bias. Unsatisfactory results were also at the highest concentration of SO_2 and NO, which could be considered valid due to large reported uncertainty.

Laboratory P had unsatisfactory results for some concentration levels of SO_2, NO and NO_2.

In other realizations of O_3 to NO_2 comparisons [25] [26], where O_3 was traceable to international standards implementing ultraviolet photometry method and NO_2 was traceable to NO international standards and GPT method was applied, a significant difference of about 2% was confirmed. At this IE, this difference can not be confirmed by individual participants, due to significant uncertainties attributed to O_3 and NO_2 measurements, but in the general evaluation a difference of 1,3% is observed between group average NO_2 and average O_3.

8. Conclusions

The proficiency evaluation scheme has provided separated assessment of participants measured values and their evaluated uncertainties. In terms of the criteria imposed by European Commission (σp) 65% of results reported by AQUILA laboratories fall into 'a1' category and are good both in terms of measured values and evaluated uncertainties. In residual 32% of results have good measured values but the evaluated uncertainties were either too big, category 'a2' (27%), or too small, category 'a3' (5%). The relative high number of cases with the comment on big uncertainty ('a2') needs further explanation. Although the common IE criterion is confirmed to be realistic by comparison to reproducibility standard deviation obtained at this (Annex C) and other IEs [24], participants are cautious/conservative in stating uncertainty. Although this might be understood at low concentrations, it is not acceptable at high concentrations, where European standards pose requirements for uncertainty. In that sense especially 'a2' results at high concentration levels should be investigated. This is especially the case for laboratories F, K and L which in the IE questionnaire expressed calibration capabilities or use of travelling standards that are not fit-for purpose (U>5%).

Four laboratories have overall unsatisfactory results of the z'-score evaluation (one bad, categories 'a6' or 'a7', or two questionable, categories 'a4' or 'a5', result per parameter) which in the view of AQUILA requires participation to the next IE in order to demonstrate remediation measures.

The comparability of results among AQUILA participants is best for O_3 and worse for NO_2 measurement method. The relative reproducibility limits, at the highest studied concentration levels, are 7.3% for SO_2, 5.4% for CO, 2.7% for O_3 and 5.3% for NO which are all below the objective derived from criteria imposed by European Commission (σp). This is not the case for NO_2 where relative reproducibility limit is 8.9% and the objective is 8.3% and is therefore unsatisfactory. For the case of NO_2 further harmonization to improve comparability among NRLs is needed.

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Annex A. Assigned values

The assigned values of tested concentration levels were derived from ERLAPs measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [17].

ERLAPs SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [10]. A different number (4 for SO_2, 7 for CO and 5 for NO) of reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [12]. All flows were measured with a certified volumeter. For the evaluation of concentration values and the uncertainties of reference gas mixtures and the evaluation of calibrations two computer applications were used, the "GUM WORKBENCH" [27] and "B-least" [28] respectively. For extending calibration from the NO to NO_2 channel of NO_X analyser, two additional calibrations/tests were preformed. First, the NO_2-converter was "bridged" (NO_2-converter was disconnected and in its place a Teflon tube was inserted) and at different NO concentration levels the NO_X channel was calibrated against the NO channel. Secondly, the GPT test was performed to establish the efficiency of NO_2-converter. For IEs test gas concentration levels ERLAPs NO_2 measurements were evaluated by the following equation:

$$[NO_2] = \frac{k \cdot (a \cdot [NO_X] + b - [NO])}{\alpha} \qquad (5)$$

Where 'a' and 'b' denote parameters from the linear calibration of NO_X channel against NO channel, 'k' denotes the slope of linear calibration of NO channel against NO reference gas mixtures and 'α' denotes the efficiency of NO_2-converter. In the evaluation of NO_2 uncertainty all these quantities have insignificant correlation. For O_3 measurements, the primary standard was used.

ERLAP's measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participating NRLs, applying the robust method described in the Annex C of ISO 13528 [17]. The validation is taking in account ERLAP's value (X) and its standard uncertainty ($u_{X'}$) as given in expression 6 [17]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_{X'}^2}} < 2 \qquad (6)$$

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of NRLs.

In Table 6 all inputs for expression 6 are given and all ERLAP's measurement results are confirmed to be valid.

Table 6: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 6.

run	unit	X	uX'	x*	s*	val.	run	unit	X	uX'	x*	s*	val.
CO _0	µmol/mol	0,484	0,023	0,48	0,08	OK	NO _10	nmol/mol	2,8	0,4	2,7	0,4	OK
CO _5	µmol/mol	1,370	0,076	1,43	0,17	OK	NO _0	nmol/mol	3,7	0,7	3,4	0,3	OK
CO _4	µmol/mol	2,408	0,067	2,48	0,16	OK	NO _9	nmol/mol	14,7	0,3	14,7	0,6	OK
CO _3	µmol/mol	4,596	0,059	4,65	0,14	OK	NO _8	nmol/mol	28,5	0,4	28,4	0,4	OK
CO _2	µmol/mol	6,183	0,050	6,22	0,13	OK	NO _7	nmol/mol	49,2	0,5	49,0	1,3	OK
CO _1	µmol/mol	8,369	0,050	8,37	0,17	OK	NO _6	nmol/mol	88,3	0,7	89,1	1,3	OK
O3 _0	nmol/mol	0,3	1,0	0,3	0,5	OK	NO _5	nmol/mol	145,7	1,1	146,6	2,5	OK
O3 _5	nmol/mol	14,3	1,0	14,0	0,5	OK	NO _4	nmol/mol	142,3	1,3	144,2	2,7	OK
O3 _3	nmol/mol	57,6	1,1	57,5	0,4	OK	NO _3	nmol/mol	241,9	1,8	244,5	5,6	OK
O3 _2	nmol/mol	99,1	1,1	99,1	0,5	OK	NO _1	nmol/mol	483,9	3,4	490,8	9,6	OK
O3 _1	nmol/mol	114,3	1,2	114,0	0,6	OK	NO2 _0	nmol/mol	0,3	0,9	0,0	0,4	OK
SO2 _0	nmol/mol	0,7	0,5	0,2	0,4	OK	NO2 _10	nmol/mol	12,8	0,3	12,3	0,9	OK
SO2 _5	nmol/mol	3,1	0,4	2,8	0,5	OK	NO2 _8	nmol/mol	21,7	0,4	21,0	1,3	OK
SO2 _4	nmol/mol	7,3	0,5	6,9	0,5	OK	NO2 _6	nmol/mol	59,1	0,8	58,3	2,2	OK
SO2 _3	nmol/mol	17,7	0,5	17,2	0,5	OK	NO2 _4	nmol/mol	102,4	1,6	101,7	3,1	OK
SO2 _2	nmol/mol	45,4	0,7	44,5	0,9	OK	NO2 _2	nmol/mol	119,7	2,4	119,5	3,5	OK
SO2 _1	nmol/mol	123,8	1,5	122,6	1,7	OK	NO2 _9	nmol/mol	0,7	0,2	0,4	0,5	OK
							NO2 _7	nmol/mol	1,0	0,3	0,7	0,4	OK
							NO2 _5	nmol/mol	1,3	0,5	1,1	0,7	OK
							NO2 _3	nmol/mol	2,1	1,0	1,9	1,1	OK
							NO2 _1	nmol/mol	4,1	1,7	4,3	1,2	OK

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. These measurements were done by LANUV during the IE with four repetitions at each concentration level. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. Relative standard uncertainty of test gas due to lack of homogeneity are given in Table 7.

Table 7: Relative standard uncertainty of test gas due to lack of homogeneity.

parameter	rel. $u_{homoginity}$ (%)
CO	0,6
O3	0,45
SO2	4
NO	1,4
NO2	1

The standard uncertainties of assigned/reference values (u_X) were calculated with equation 7 and used in the proficiency evaluations of chapter 5.

$$u_X^2 = u_{X'}^2 + \left(X \cdot u_{\text{hom}\,oginety}\right)^2 \qquad (7)$$

Annex B. Results of the IE

The reported values, presented also in graphs, are given in this annex. The participants were asked to report results (x_{ij}, $u(x_i)$ and $U(x_i)$) expressed in mol/mol units. For all the runs except concentration levels 0, also each participant's average (x_i) and standard deviation (s_i) are presented. As a group evaluation robust average (x*) and robust standard deviation (s*) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following tables. The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ($U(x_i)$) are indicated with error bars.

Reported values for SO_2

Table 8: Reported values for SO_2 concentration level 0.

parameter: SO2 level: 0	all units are nmol/mol	x*: 0.23	s*: 0.40											
	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	0.3	0.14	-0.1	-0.18	0.03	0.26	-0.75	0.09	1.176	0.10	0.95	0.70	0.74	0.11	-0.10
u(xi)	0.3	0.43	0.10	1.157	1.00	0.04	0.90	0.77	0.02	0.50	0.05	1.50	0.46	0.70	0.004
U(xi)	0.5	0.85	0.20	2.315	1.96	0.07	1.80	1.60	0.04	1.00	0.1	3.00	0.92	1.40	0.008

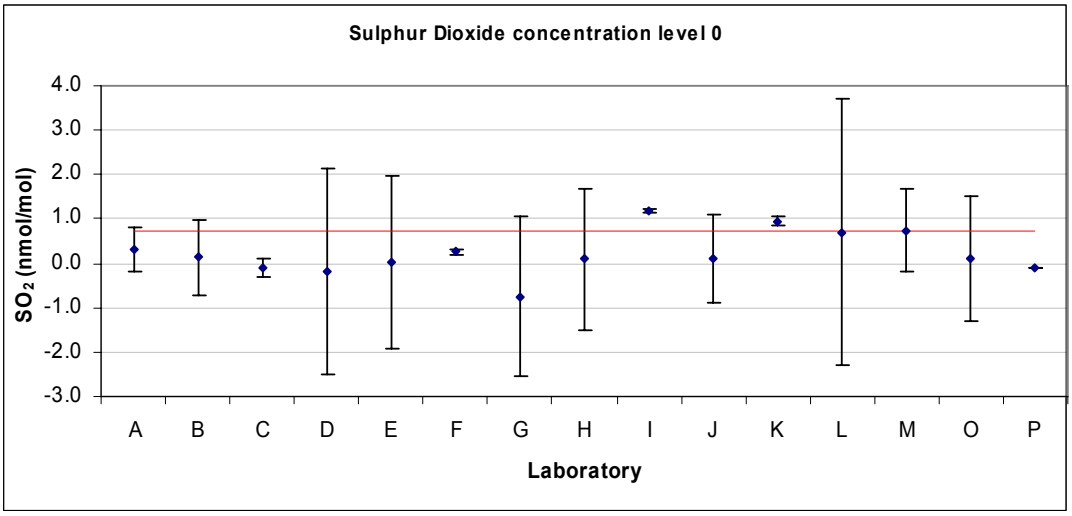

Figure 13: Reported values for SO_2 concentration level 0.

Table 9: Reported values for SO_2 concentration level 1.

parameter: SO2 level: 1 all units are nmol/mol x*: 122.55 s*: 1.72

	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	120.9	119.08	123.5	122.0	123.43	127.87	123.4	119.74	123.26	123.80	121.08	115.91	123.76	136.71	111.12
xi,2	121.2	119.26	123.4	122.1	123.66	127.94	123.1	119.89	123.49	124.00	121.31	116.11	123.78	136.65	110.82
xi,3	121.2	119.16	123.4	122.2	124.03	128.00	123.2	120.30	123.26	124.00	121.22	115.90	123.95	137.11	111.53
xi	121.10	119.167	123.43	122.10	123.707	127.937	123.23	119.977	123.337	123.933	121.203	115.973	123.830	136.823	111.157
si	0.17	0.090	0.06	0.10	0.303	0.065	0.15	0.290	0.133	0.115	0.116	0.118	0.104	0.250	0.356
u(xi)	1.3	2.63	1.24	2.195	2.99	2.88	2.9	1.64	2.35	2.31	3	4.50	1.52	3.42	5.08
U(xi)	2.5	5.26	2.47	4.390	5.87	5.77	5.7	3.30	4.69	4.62	7	9.00	3.04	6.84	10.16

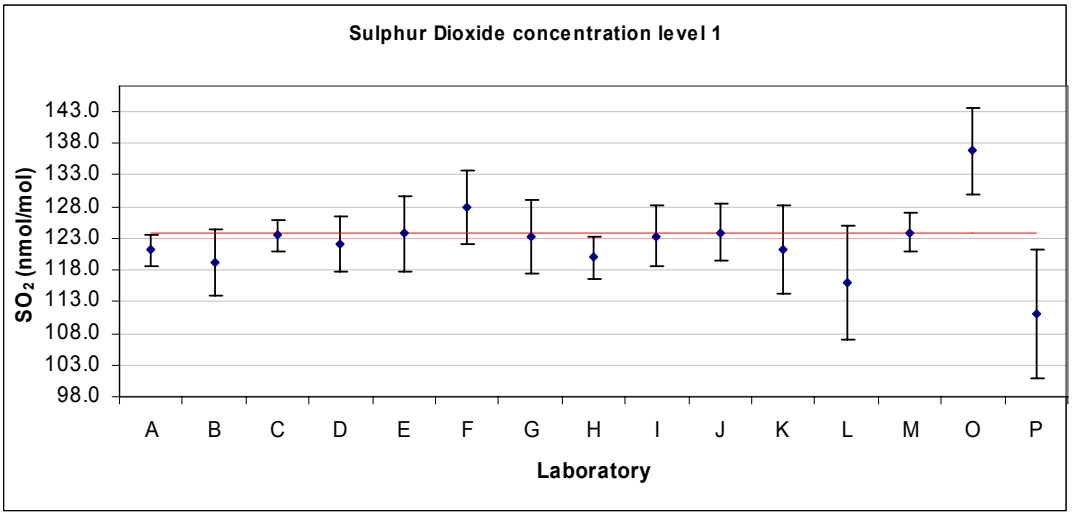

Figure 14: Reported values for SO_2 concentration level 1.

Table 10: Reported values for SO_2 concentration level 2.

parameter: SO2 level: 2 all units are nmol/mol x*: 44.53 s*: 0.90

	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	44.3	43.61	44.2	44.21	44.71	46.57	44.4	43.65	45.70	45.10	44.28	42.44	45.55	49.85	40.75
xi,2	44.2	43.24	44.6	44.04	44.71	46.76	44.6	43.75	46.00	45.00	44.51	42.57	45.27	49.86	40.25
xi,3	44.5	43.23	44.8	43.99	44.74	46.65	44.6	43.75	45.82	45.10	44.34	42.58	45.28	49.81	40.36
xi	44.33	43.360	44.53	44.080	44.720	46.660	44.53	43.717	45.840	45.067	44.377	42.530	45.367	49.840	40.453
si	0.15	0.217	0.31	0.115	0.017	0.095	0.12	0.058	0.151	0.058	0.119	0.078	0.159	0.026	0.263
u(xi)	0.5	1.06	0.51	1.533	1.43	1.06	1.3	0.79	0.87	0.84	1	2.51	0.69	1.50	1.80
U(xi)	1.0	2.12	1.02	3.066	2.80	2.11	2.5	1.60	1.74	1.68	2	5.02	1.38	2.99	3.60

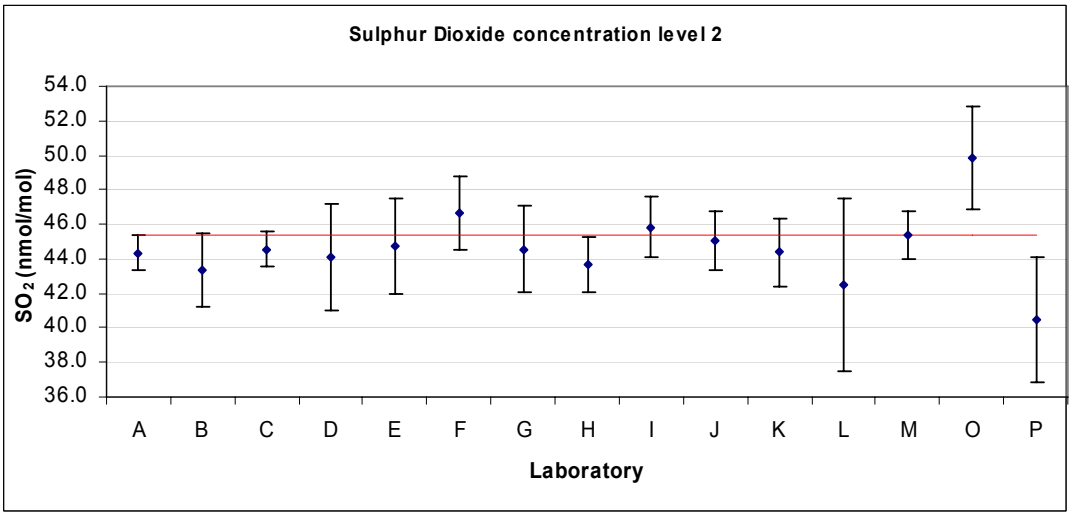

Figure 15: Reported values for SO_2 concentration level 2.

Table 11: Reported values for SO_2 concentration level 3.

parameter: SO2	level: 3	all units are nmol/mol	x*: 17.16	s*: 0.52

	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	17.2	16.60	17.0	16.68	16.77	18.02	16.6	16.66	18.00	17.20	17.52	16.67	17.61	19.00	15.30
xi,2	17.3	16.68	17.1	16.83	16.86	17.98	16.7	16.69	18.36	17.30	17.54	16.72	17.57	19.15	15.61
xi,3	17.2	16.69	17.1	16.85	17.03	18.05	16.9	16.71	18.51	17.40	17.51	16.73	17.87	19.24	16.30
xi	17.23	16.657	17.07	16.787	16.887	18.017	16.73	16.687	18.290	17.300	17.523	16.707	17.683	19.130	15.737
si	0.06	0.049	0.06	0.093	0.132	0.035	0.15	0.025	0.262	0.100	0.015	0.032	0.163	0.121	0.512
u(xi)	0.3	0.61	0.17	1.301	1.07	0.41	0.9	0.71	0.35	0.37	0.5	1.82	0.50	1.15	0.70
U(xi)	0.5	1.22	0.40	2.603	2.10	0.83	1.8	1.50	0.70	0.74	0.9	3.64	1.00	2.30	1.40

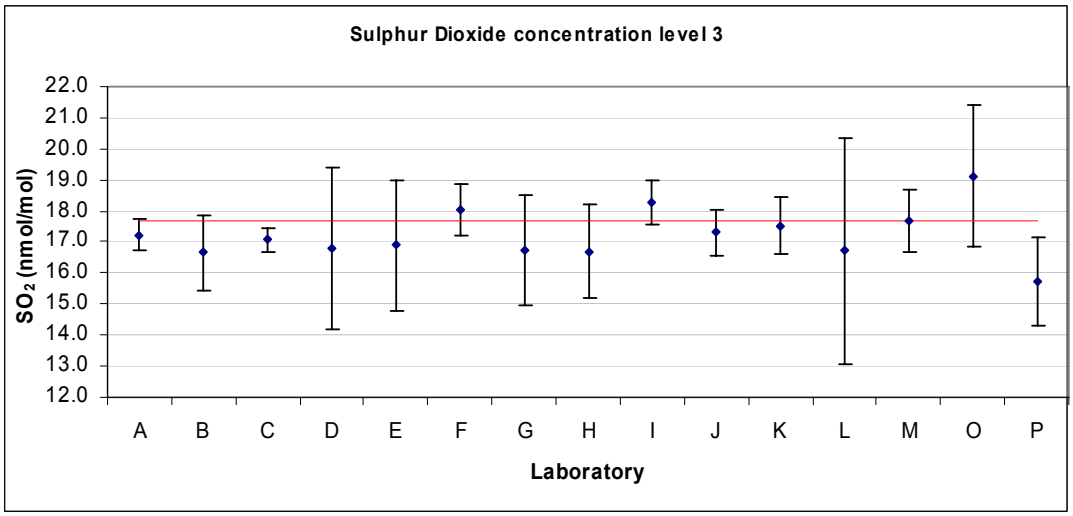

Figure 16: Reported values for SO_2 concentration level 3.

Table 12: Reported values for SO_2 concentration level 4.

parameter: SO2	level: 4	all units are nmol/mol	x*: 6.86	s*: 0.49

	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	7.0	6.72	6.7	6.267	6.46	7.36	6.3	6.64	8.16	6.90	7.42	6.92	7.34	7.62	6.03
xi,2	7.2	6.59	6.6	6.392	6.48	7.22	6.3	6.60	8.12	6.80	7.24	6.82	7.34	7.65	5.91
xi,3	7.1	6.62	6.6	6.287	6.39	7.24	6.1	6.61	7.90	6.80	7.17	7.04	7.33	7.58	5.92
xi	7.10	6.643	6.63	6.3153	6.443	7.273	6.23	6.617	8.060	6.833	7.277	6.927	7.337	7.617	5.953
si	0.10	0.068	0.06	0.0671	0.047	0.076	0.12	0.021	0.140	0.058	0.129	0.110	0.006	0.035	0.067
u(xi)	0.3	0.47	0.07	1.212	1.01	0.18	0.8	0.74	0.16	0.27	0.2	1.56	0.45	0.95	0.35
U(xi)	0.5	0.93	0.20	2.425	1.98	0.35	1.6	1.50	0.31	0.54	0.4	3.12	0.90	1.90	0.67

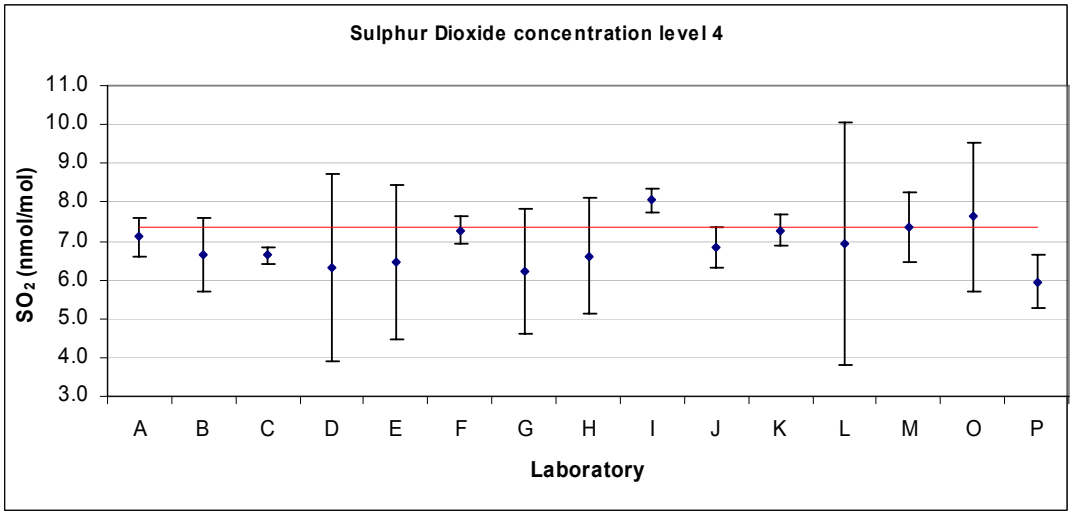

Figure 17: Reported values for SO_2 concentration level 4.

Table 13: Reported values for SO_2 concentration level 5.

parameter: SO2	level: 5	all units are nmol/mol								x*: 2.78		s*: 0.55			
	A	B	C	D	E	F	G	H	I	J	K	L	M	O	P
xi,1	3.0	2.68	2.5	2.171	2.23	2.98	1.6	2.55	3.91	2.70	3.38	3.20	3.12	3.06	2.35
xi,2	3.1	2.67	2.5	2.284	2.28	2.89	1.4	2.51	4.00	2.70	3.27	3.19	3.20	3.01	2.16
xi,3	3.1	2.67	2.5	2.293	2.26	2.94	1.3	2.49	4.03	2.70	3.37	3.20	3.05	3.04	2.15
xi	3.07	2.673	2.50	2.2493	2.257	2.937	1.43	2.517	3.980	2.700	3.340	3.197	3.123	3.037	2.220
si	0.06	0.006	0.00	0.0680	0.025	0.045	0.15	0.031	0.062	0.000	0.061	0.006	0.075	0.025	0.113
u(xi)	0.3	0.45	0.10	1.178	1.00	0.09	0.9	0.75	0.08	0.24	0.09	1.50	0.38	0.90	0.11
U(xi)	0.5	0.90	0.20	2.356	1.96	0.19	1.8	1.50	0.15	0.48	0.2	3.00	0.76	1.80	0.21

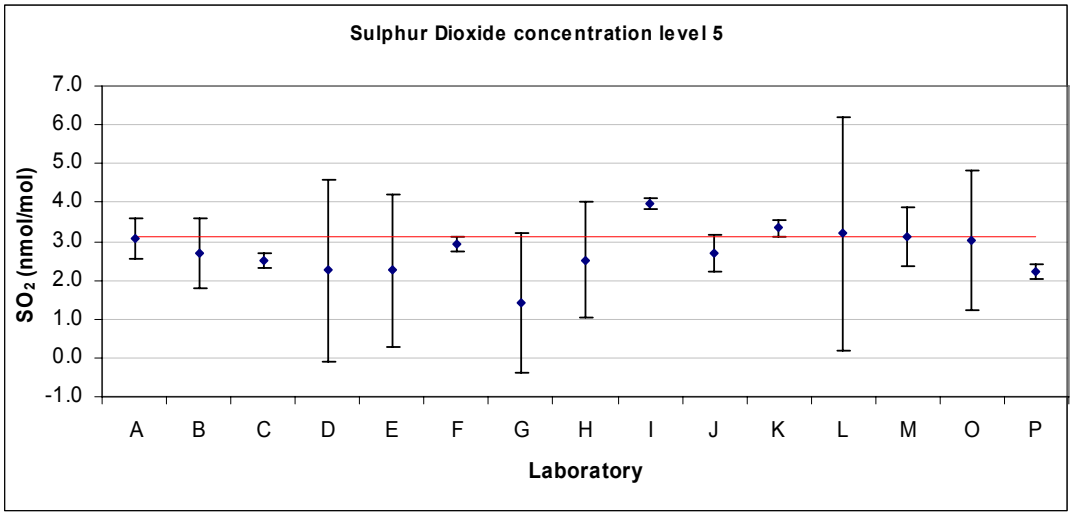

Figure 18: Reported values for SO_2 concentration level 5.

Reported values for CO

Table 14: Reported values for CO concentration level 0.

parameter: CO	level: 0	all units are µmol/mol								x*: 0.476		s*: 0.081		
	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	0.50	0.881	0.50	0.414	0.69	0.453	0.48	0.53	0.0088	0.05	0.18	0.509	0.484	0.168
u(xi)	0.01	0.060	0.010	0.144	0.05	0.014	0.06	0.06	0.0002	0.06	0.05	0.541	0.023	0.050
U(xi)	0.02	0.121	0.020	0.289	0.10	0.029	0.12	0.12	0.0003	0.12	0.1	1.082	0.046	0.100

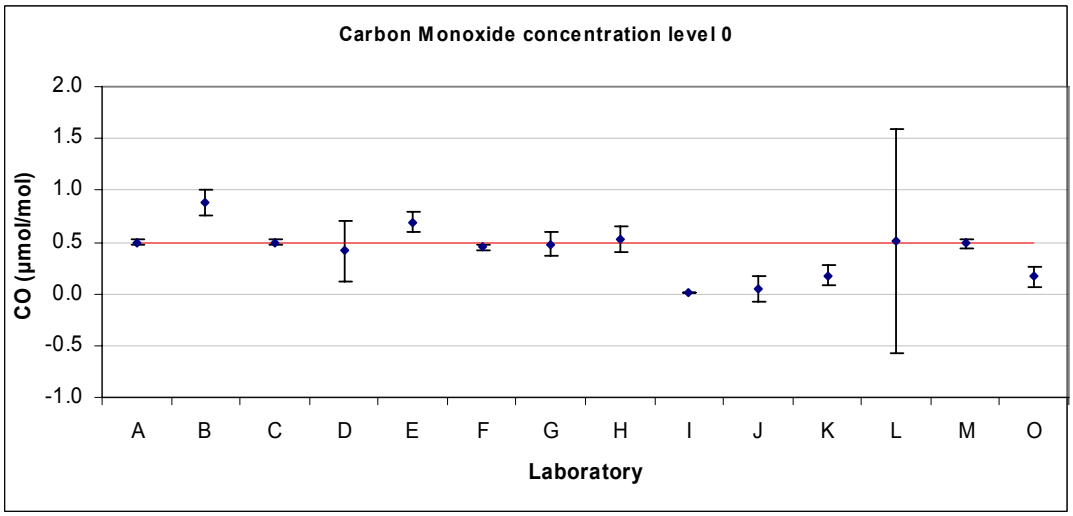

Figure 19: Reported values for CO concentration level 0.

Table 15: Reported values for CO concentration level 1.

parameter: CO	level: 1	all units are µmol/mol	x*: 8.374	s*: 0.166

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	8.53	8.263	8.34	8.382	8.35	8.566	8.52	8.54	8.088	7.82	8.46	8.384	8.375	7.657
xi,2	8.52	8.232	8.33	8.362	8.35	8.563	8.52	8.53	8.096	7.82	8.46	8.374	8.370	7.662
xi,3	8.52	8.226	8.31	8.328	8.34	8.561	8.51	8.53	8.106	7.81	8.46	8.363	8.361	7.659
xi	8.523	8.2403	8.327	8.3573	8.347	8.5633	8.517	8.533	8.0967	7.817	8.460	8.3737	8.3687	7.6593
si	0.006	0.0199	0.015	0.0273	0.006	0.0025	0.006	0.006	0.0090	0.006	0.000	0.0105	0.0071	0.0025
u(xi)	0.09	0.188	0.083	0.191	0.20	0.463	0.21	0.08	0.150	0.11	0.2	0.633	0.050	0.250
U(xi)	0.17	0.376	0.167	0.383	0.39	0.926	0.42	0.15	0.300	0.22	0.4	1.266	0.100	0.500

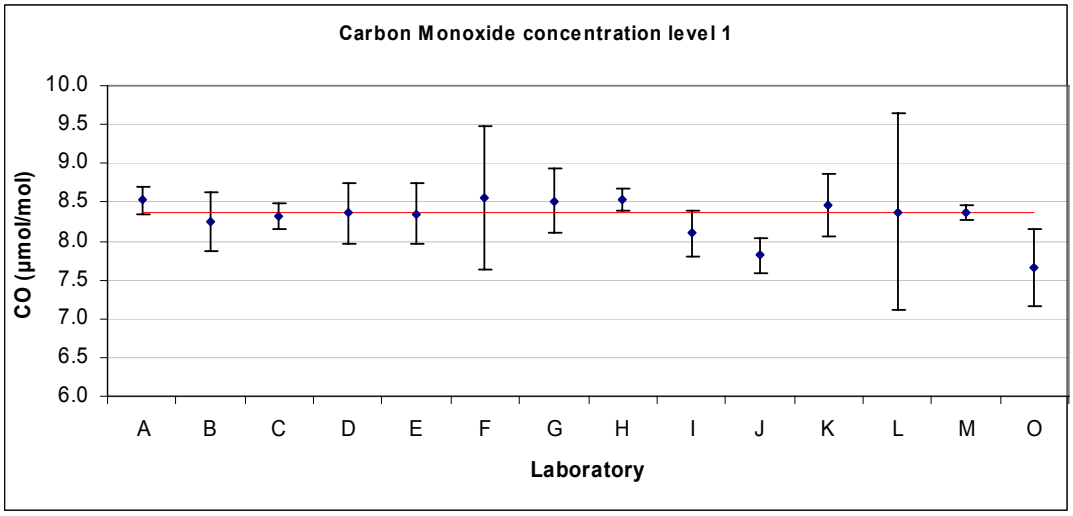

Figure 20: Reported values for CO concentration level 1.

Table 16: Reported values for CO concentration level 2.

parameter: CO	level: 2	all units are µmol/mol	x*: 6.217	s*: 0.125

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	6.29	6.256	6.17	6.056	6.25	6.333	6.30	6.32	5.965	5.67	6.21	6.203	6.166	5.635
xi,2	6.30	6.250	6.18	6.091	6.26	6.359	6.34	6.35	5.994	5.71	6.19	6.223	6.183	5.666
xi,3	6.32	6.262	6.20	6.085	6.28	6.387	6.35	6.39	6.027	5.71	6.22	6.239	6.201	5.682
xi	6.303	6.2560	6.183	6.0773	6.263	6.3597	6.330	6.353	5.9953	5.697	6.207	6.2217	6.1833	5.6610
si	0.015	0.0060	0.015	0.0187	0.015	0.0270	0.026	0.035	0.0310	0.023	0.015	0.0180	0.0175	0.0239
u(xi)	0.07	0.148	0.062	0.178	0.15	0.344	0.16	0.06	0.111	0.08	0.2	0.607	0.050	0.180
U(xi)	0.13	0.296	0.124	0.356	0.30	0.687	0.32	0.12	0.222	0.16	0.3	1.214	0.100	0.360

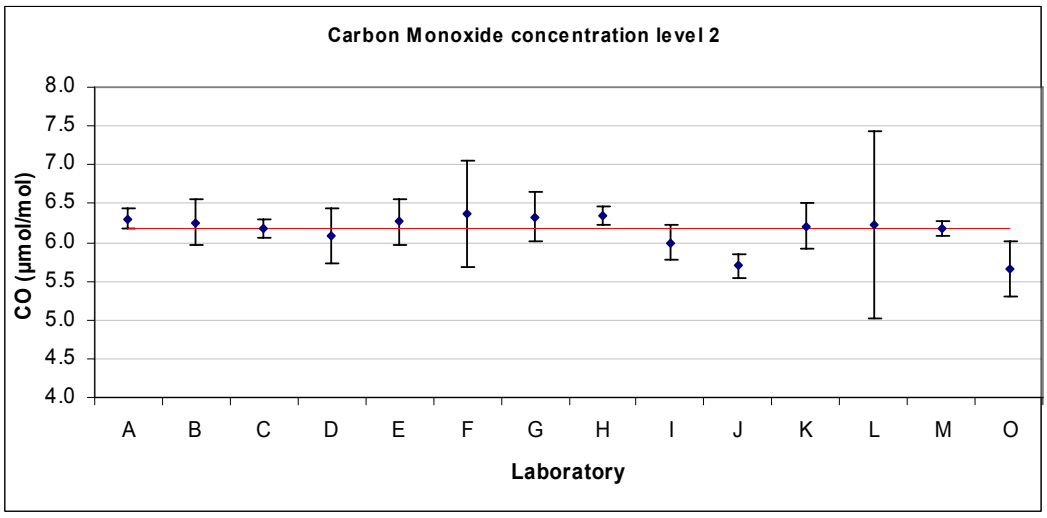

Figure 21: Reported values for CO concentration level 2.

Table 17: Reported values for CO concentration level 3.

parameter: CO	level: 3	all units are µmol/mol	x*: 4.646	s*: 0.137

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	4.66	4.743	4.63	4.497	4.71	4.741	4.74	4.80	4.446	4.14	4.51	4.640	4.574	4.159
xi,2	4.68	4.775	4.64	4.521	4.72	4.747	4.74	4.82	4.470	4.16	4.53	4.657	4.590	4.181
xi,3	4.71	4.791	4.66	4.543	4.75	4.783	4.75	4.87	4.510	4.21	4.57	4.692	4.623	4.216
xi	4.683	4.7697	4.643	4.5203	4.727	4.7570	4.743	4.830	4.4753	4.170	4.537	4.6630	4.5957	4.1853
si	0.025	0.0244	0.015	0.0230	0.021	0.0227	0.006	0.036	0.0323	0.036	0.031	0.0265	0.0250	0.0287
u(xi)	0.05	0.120	0.047	0.169	0.12	0.257	0.12	0.06	0.083	0.06	0.1	0.589	0.059	0.130
U(xi)	0.09	0.239	0.093	0.337	0.23	0.514	0.24	0.11	0.166	0.12	0.2	1.178	0.118	0.260

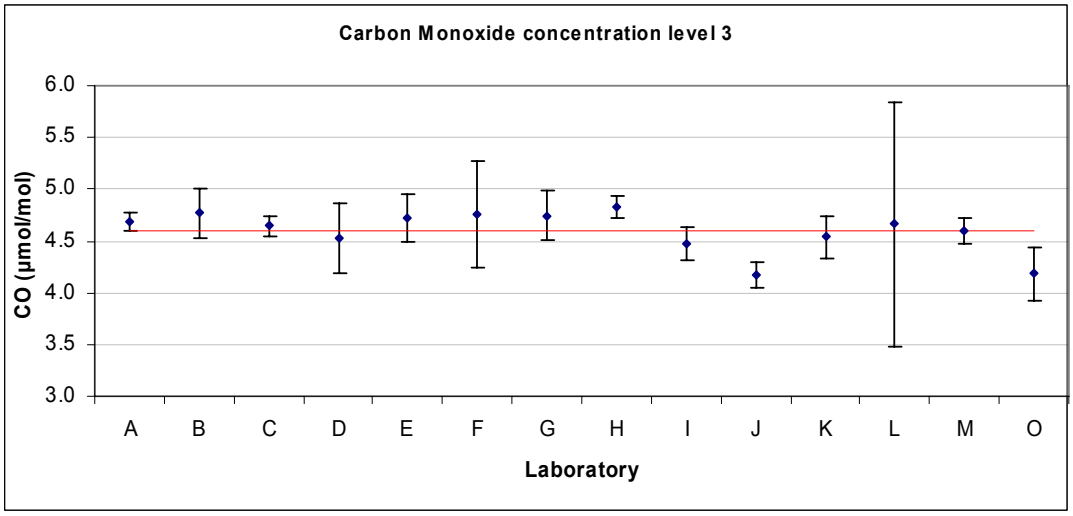

Figure 22: Reported values for CO concentration level 3.

Table 18: Reported values for CO concentration level 4.

parameter: CO	level: 4	all units are µmol/mol	x*: 2.477	s*: 0.164

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	2.47	2.824	2.51	2.403	2.68	2.555	2.52	2.66	2.359	2.10	2.27	2.532	2.428	2.141
xi,2	2.45	2.801	2.50	2.387	2.65	2.545	2.47	2.65	2.355	2.11	2.26	2.518	2.405	2.128
xi,3	2.44	2.793	2.48	2.364	2.64	2.542	2.47	2.65	2.358	2.11	2.24	2.511	2.392	2.126
xi	2.453	2.8060	2.497	2.3847	2.657	2.5473	2.487	2.653	2.3573	2.107	2.257	2.5203	2.4083	2.1317
si	0.015	0.0161	0.015	0.0196	0.021	0.0068	0.029	0.006	0.0021	0.006	0.015	0.0107	0.0182	0.0081
u(xi)	0.03	0.086	0.025	0.156	0.08	0.138	0.07	0.06	0.044	0.04	0.06	0.564	0.067	0.080
U(xi)	0.05	0.171	0.050	0.312	0.15	0.275	0.14	0.11	0.087	0.08	0.1	1.128	0.134	0.160

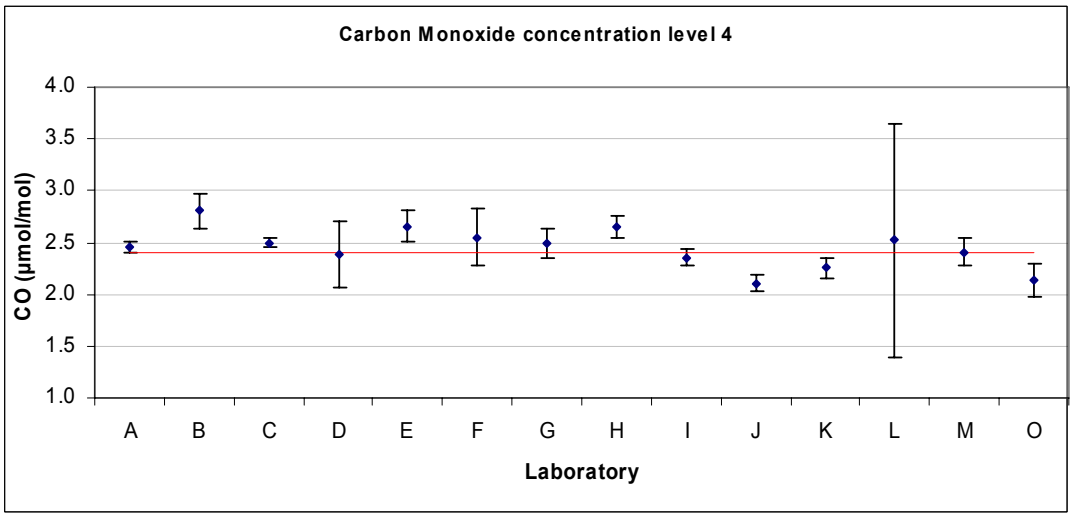

Figure 23: Reported values for CO concentration level 4.

Table 19: Reported values for CO concentration level 5.

parameter: CO	level: 5	all units are µmol/mol	x*: 1.425	s*: 0.172

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	1.41	1.801	1.41	1.360	1.62	1.524	1.44	1.65	1.363	1.19	1.17	1.516	1.386	1.088
xi,2	1.38	1.778	1.38	1.321	1.58	1.502	1.41	1.62	1.333	1.19	1.12	1.492	1.354	1.066
xi,3	1.39	1.739	1.36	1.353	1.58	1.524	1.43	1.65	1.374	1.19	1.16	1.508	1.370	1.096
xi	1.393	1.7727	1.383	1.3447	1.593	1.5167	1.427	1.640	1.3567	1.190	1.150	1.5053	1.3700	1.0833
si	0.015	0.0313	0.025	0.0208	0.023	0.0127	0.015	0.017	0.0212	0.000	0.026	0.0122	0.0160	0.0155
u(xi)	0.02	0.072	0.014	0.150	0.06	0.082	0.06	0.06	0.025	0.04	0.05	0.552	0.076	0.060
U(xi)	0.03	0.143	0.029	0.300	0.12	0.164	0.12	0.11	0.050	0.08	0.1	1.105	0.152	0.120

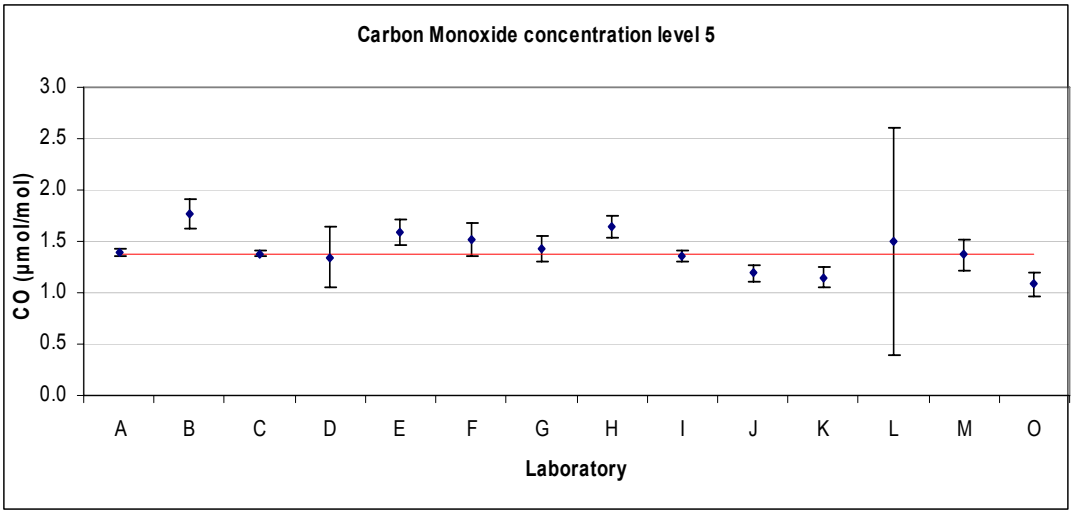

Figure 24: Reported values for CO concentration level 5.

Reported values for O_3

Table 20: Reported values for O3 concentration level 0.

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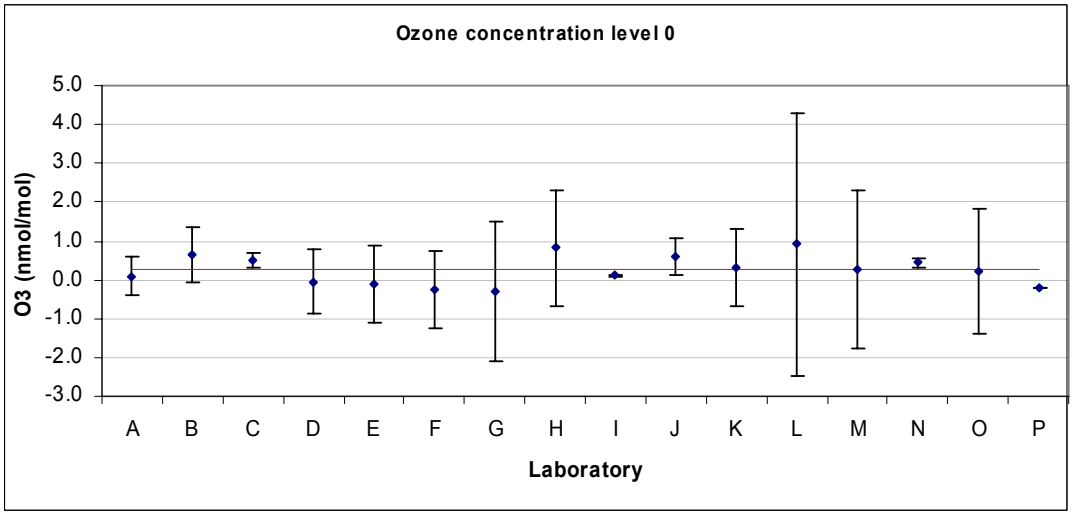

Figure 25: Reported values for O3 concentration level 0.

Table 21: Reported values for O3 concentration level 1.

parameter: O3 level: 1 all units are nmol/mol x*: 114.02 s*: 0.62

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	113.4	112.84	113.9	112.5	111.85	114.59	111.9	112.87	113.32	112.10	112.71	113.74	113.69	119.1	110.50	114.25
xi,2	114.4	113.96	114.8	113.4	113.46	115.87	112.9	114.28	114.61	114.90	113.62	114.82	114.63	123.0	114.19	115.61
xi,3	115.0	114.14	114.9	113.5	113.83	115.89	112.9	114.37	114.73	116.50	113.69	114.87	114.62	118.5	115.79	115.25
xi	114.27	113.647	114.53	113.13	113.047	115.450	112.57	113.840	114.220	114.500	113.340	114.477	114.313	120.20	113.493	115.037
si	0.81	0.704	0.55	0.55	1.053	0.745	0.58	0.841	0.782	2.227	0.547	0.638	0.540	2.44	2.713	0.705
u(xi)	1.2	1.48	1.3	1.35	2.32	2.47	2.4	1.72	3.66	1.77	3	2.43	1.18	1.50	3.88	4.03
U(xi)	2.3	2.96	2.7	2.700	4.54	4.94	4.7	3.50	7.31	3.54	6	4.86	2.36	3.15	7.75	8.06

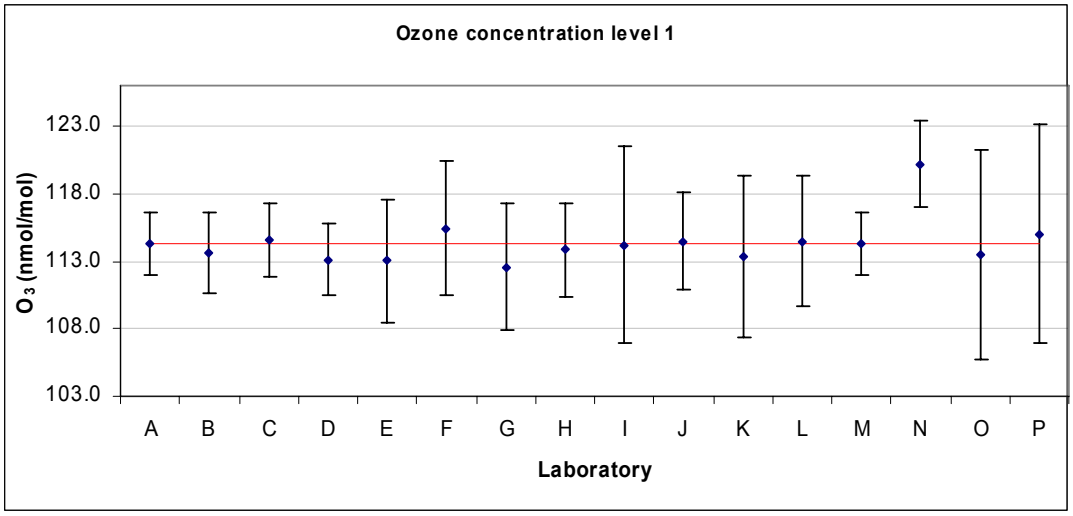

Figure 26: Reported values for O3 concentration level 1.

Table 22: Reported values for O3 concentration level 2.

parameter: O3 level: 2 all units are nmol/mol x*: 99.08 s*: 0.55

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	98.9	98.62	99.4	97.66	98.57	100.09	97.0	98.98	98.83	101.70	97.85	99.23	98.91	103.0	101.35	99.73
xi,2	99.3	98.90	99.4	97.81	98.94	100.24	97.2	99.20	98.96	102.60	97.99	99.35	99.08	107.9	102.35	99.92
xi,3	99.5	99.11	99.7	98.04	99.18	100.53	97.5	99.55	99.43	103.40	98.24	99.62	99.28	102.8	102.98	100.11
xi	99.23	98.877	99.50	97.837	98.897	100.287	97.23	99.243	99.073	102.567	98.027	99.400	99.090	104.57	102.227	99.920
si	0.31	0.246	0.17	0.191	0.307	0.224	0.25	0.287	0.316	0.850	0.198	0.200	0.185	2.89	0.822	0.190
u(xi)	1.0	1.29	1.0	1.22	2.04	2.26	2.1	1.49	3.17	1.61	3	2.27	1.10	1.61	3.49	2.99
U(xi)	2.0	2.58	2.0	2.441	4.00	4.51	4.1	3.00	6.34	3.22	6	4.54	2.20	3.21	6.98	6.00

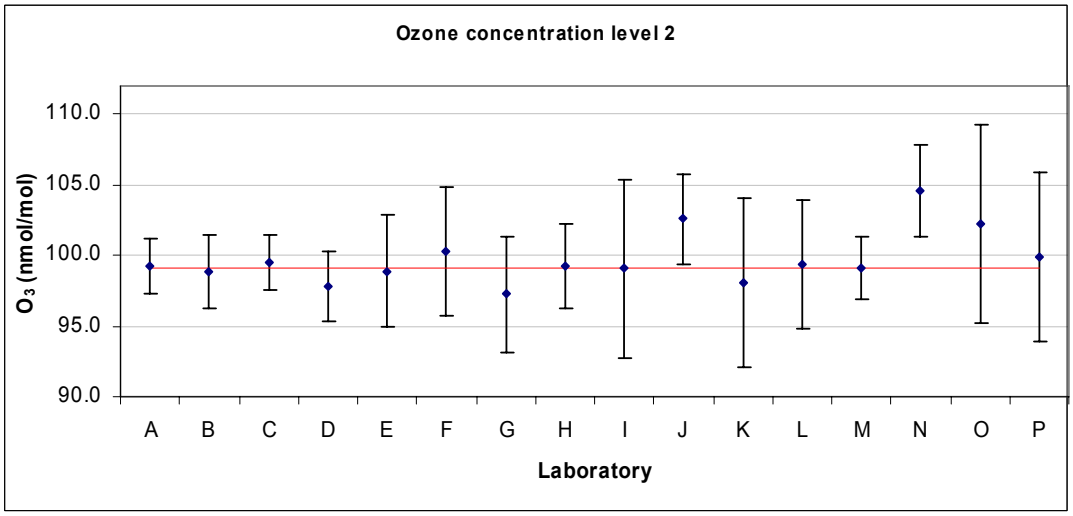

Figure 27: Reported values for O3 concentration level 2.

Table 23: Reported values for O3 concentration level 3.

parameter: O3 level: 3 all units are nmol/mol x*: 57.51 s*: 0.41

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	57.4	57.49	57.8	56.78	57.35	57.97	55.9	57.62	57.52	59.70	56.70	57.81	57.47		59.46	57.77
xi,2	57.1	57.71	58.1	56.99	57.20	56.30	56.0	57.74	57.45	60.00	55.28	57.90	57.57		59.76	56.82
xi,3	57.6	57.84	58.0	57.03	57.56	58.17	56.1	57.83	57.53	60.40	56.97	58.04	57.69	58.79	59.95	56.65
xi	57.37	57.680	57.97	56.933	57.370	57.480	56.00	57.730	57.500	60.033	56.317	57.917	57.577	58.79	59.723	57.080
si	0.25	0.177	0.15	0.134	0.181	1.027	0.10	0.105	0.044	0.351	0.908	0.116	0.110		0.247	0.604
u(xi)	0.6	0.87	1.0	0.886	1.25	2.03	1.2	1.04	1.84	0.95	2	1.90	1.06	2.33	2.04	1.82
U(xi)	1.2	1.73	2.0	1.773	2.45	4.06	2.4	2.10	3.68	1.90	3	3.81	2.12	4.45	4.08	3.64

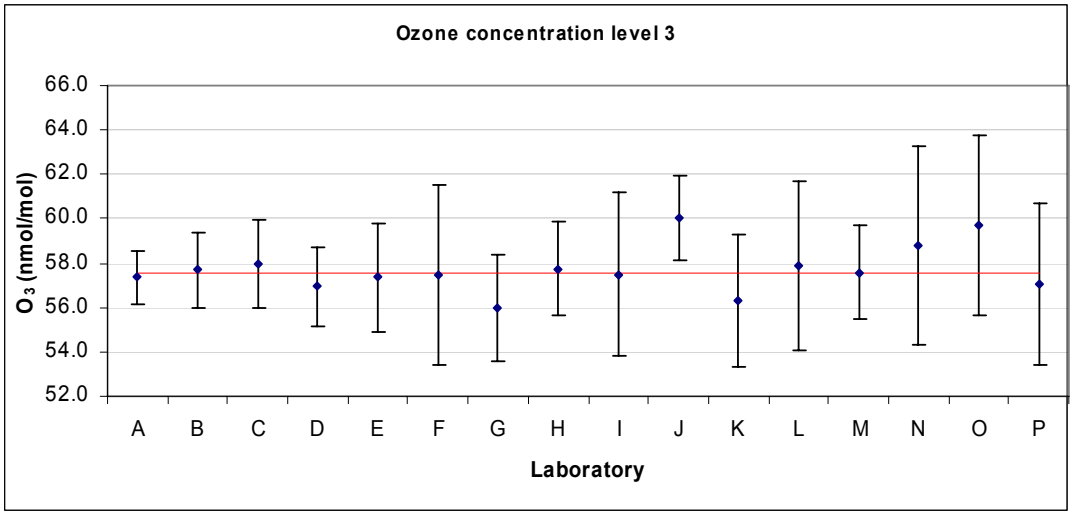

Figure 28: Reported values for O3 concentration level 3.

Table 24: Reported values for O3 concentration level 5.

parameter: O3 level: 5 all units are nmol/mol x*: 14.05 s*: 0.46

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	14.1	14.24	14.3	13.96	13.69	13.74	12.9	14.32	13.67	14.40	13.81	14.67	14.30	11.63	14.13	13.41
xi,2	13.9	14.19	14.3	13.94	13.64	13.74	12.9	14.39	13.42	14.90	13.87	14.57	14.33	13.54	14.16	13.82
xi,3	14.1	14.38	14.4	13.89	13.64	13.75	13.0	14.40	13.58	14.60	13.84	14.56	14.32	11.75	14.23	13.55
xi	14.03	14.270	14.33	13.930	13.657	13.743	12.93	14.370	13.557	14.633	13.840	14.600	14.317	12.307	14.173	13.593
si	0.12	0.098	0.06	0.036	0.029	0.006	0.06	0.044	0.127	0.252	0.030	0.061	0.015	1.070	0.051	0.208
u(xi)	0.2	0.37	1.0	0.532	0.57	1.06	0.9	0.76	0.44	0.23	0.5	1.70	1.02	1.52	1.09	0.50
U(xi)	0.3	0.74	2.0	1.065	1.12	2.12	1.8	1.60	0.87	0.46	1	3.40	2.04	3.04	2.18	1.00

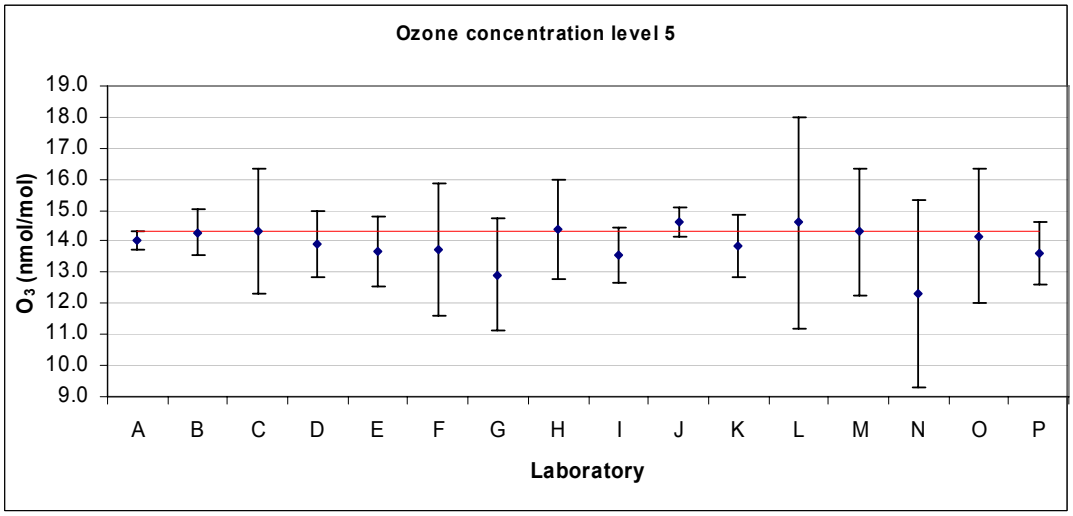

Figure 29: Reported values for O3 concentration level 5.

Reported values for NO

Table 25: Reported values for NO concentration level 0.

arameter: NO level: 0	all units are nmol/mol	x*: 3.39	s*: 0.26													
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	3.2	3.23	3.7	4.062	3.02	3.35	3.3	3.41	3.095	3.30	3.38	3.78	3.69	1.36	3.87	-0.21
u(xi)	0.3	0.38	0.10	0.573	1.00	0.04	0.9	0.75	0.06	1.38	0.5	1.50	0.70	0.33	0.75	0.005
U(xi)	0.5	0.76	0.20	1.147	1.96	0.09	1.8	1.50	0.13	2.77	1	3.00	1.41	0.73	1.50	0.01

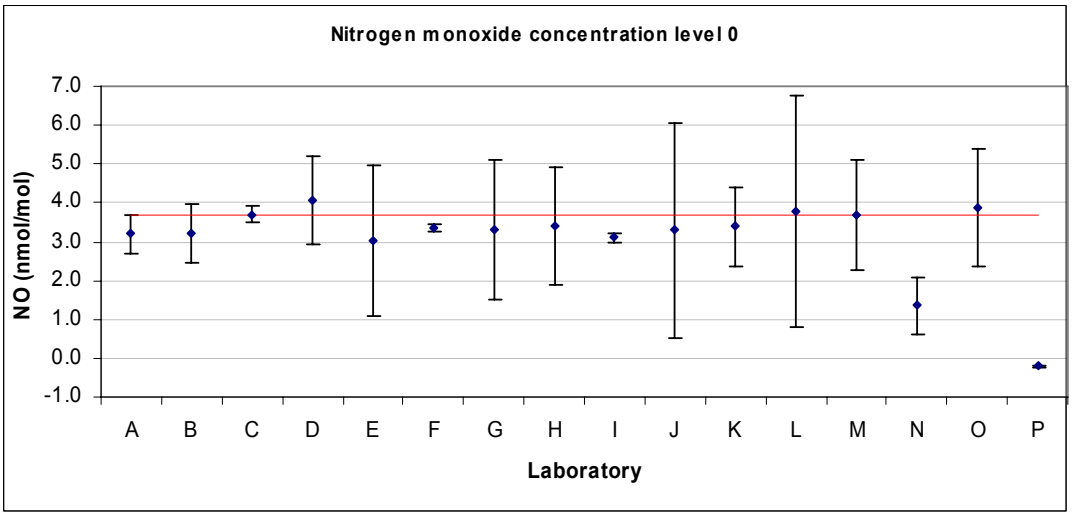

Figure 30: Reported values for NO concentration level 0.

Table 26: Reported values for NO concentration level 1.

parameter: NO	level: 1	all units are nmol/mol								x*: 490.75		s*: 9.63				
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	487.7	497.04	484.1	489.2	483.67	503.40	496.1	498.86	479.24	481.10	498.33	502.15	484.55	486.96	516.85	487.12
xi,2	487.4	496.25	484.1	490.4	481.88	503.09	495.5	498.30	478.17	481.10	497.81	501.50	483.82	489.69	516.28	486.25
xi,3	487.3	496.53	483.1	487.6	482.40	502.55	495.4	498.36	477.41	481.10	497.99	501.45	483.33	489.98	514.97	488.11
xi	487.47	496.607	483.77	489.07	482.650	503.013	495.67	498.507	478.273	481.100	498.043	501.700	483.900	488.877	516.033	487.160
si	0.21	0.401	0.58	1.40	0.921	0.430	0.38	0.307	0.919	0.000	0.264	0.391	0.614	1.666	0.964	0.931
u(xi)	4.9	10.74	5.06	6.375	11.05	16.12	13.0	5.41	9.81	6.73	13	12.27	3.44	9.1	19.35	14.61
U(xi)	9.8	21.47	10.12	12.750	21.66	32.24	26.0	10.90	19.61	13.47	25	24.54	6.89	18.7	38.70	29.23

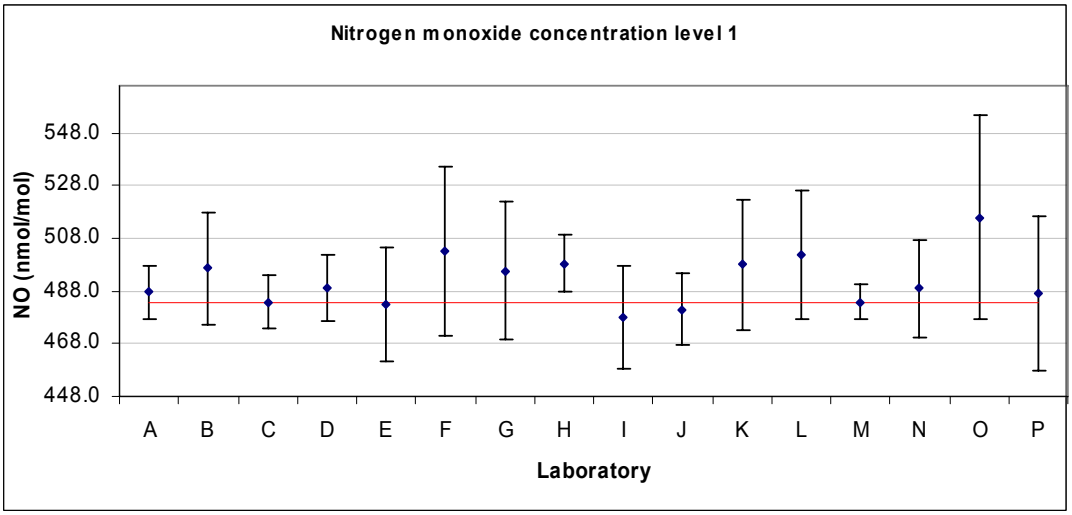

Figure 31: Reported values for NO concentration level 1.

Table 27: Reported values for NO concentration level 2.

parameter: NO level: 2 all units are nmol/mol x*: 375.48 s*: 6.07

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
xi,1	377.7	374.61	368.0	374.6	378.03	389.56	379.8	381.08	362.45	374.10	387.08	384.67	370.71	385.80	390.69
xi,2	372.4	373.52	368.7	371.5	372.29	383.70	376.9	377.39	369.96	375.10	381.81	381.67	367.63	380.61	388.67
xi,3	370.6	374.78	367.6	371.9	370.89	381.71	377.2	377.24	376.04	374.20	379.13	382.55	368.37	375.38	389.41
xi	373.57	374.303	368.10	372.67	373.737	384.990	377.97	378.570	369.483	374.467	382.673	382.963	368.903	380.597	389.590
si	3.69	0.684	0.56	1.69	3.783	4.081	1.59	2.175	6.808	0.551	4.045	1.542	1.608	5.210	1.022
u(xi)	3.8	8.10	3.89	4.983	8.58	12.34	9.0	4.08	7.58	5.24	10	9.71	3.49	3.2	14.61
U(xi)	7.5	16.19	7.77	9.966	16.82	24.67	18.0	8.30	15.15	10.48	20	19.42	6.98	7.12	29.22

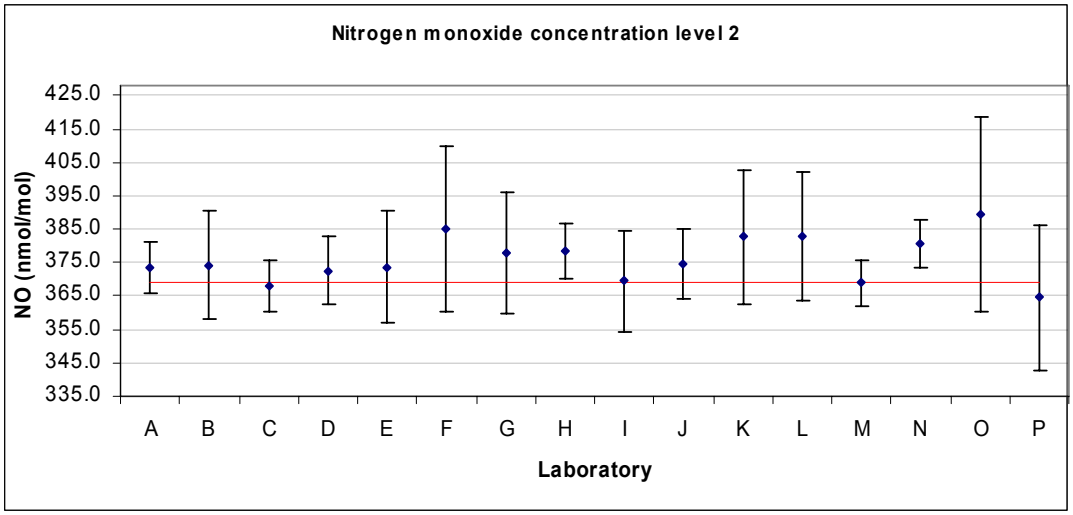

Figure 32: Reported values for NO concentration level 2.

Table 28: Reported values for NO concentration level 3.

parameter: NO level: 3 all units are nmol/mol x*: 244.47 s*: 5.64

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	242.5	242.61	240.8	244.0	240.73	251.10	251.0	246.09	235.76	238.70	247.12	251.33	241.68	243.85	254.82	241.41
xi,2	242.6	242.92	241.0	248.7	241.21	251.14	250.9	246.49	235.85	238.40	247.41	251.49	241.89	245.80	254.81	240.95
xi,3	242.7	243.06	241.2	247.6	241.24	251.28	250.9	246.52	236.01	238.50	247.84	251.64	241.99	270.61	255.03	240.72
xi	242.60	242.863	241.00	246.77	241.060	251.173	250.93	246.367	235.873	238.533	247.457	251.487	241.853	253.420	254.887	241.027
si	0.10	0.230	0.20	2.46	0.286	0.095	0.06	0.240	0.127	0.153	0.362	0.155	0.158	14.919	0.124	0.351
u(xi)	2.5	5.26	2.44	3.477	5.59	8.05	5.4	2.64	4.80	3.34	6	6.83	1.79	6.91	9.56	7.23
U(xi)	4.9	10.52	4.87	6.953	10.95	16.10	10.8	5.30	9.67	6.68	13	13.67	3.58	14.16	19.12	14.46

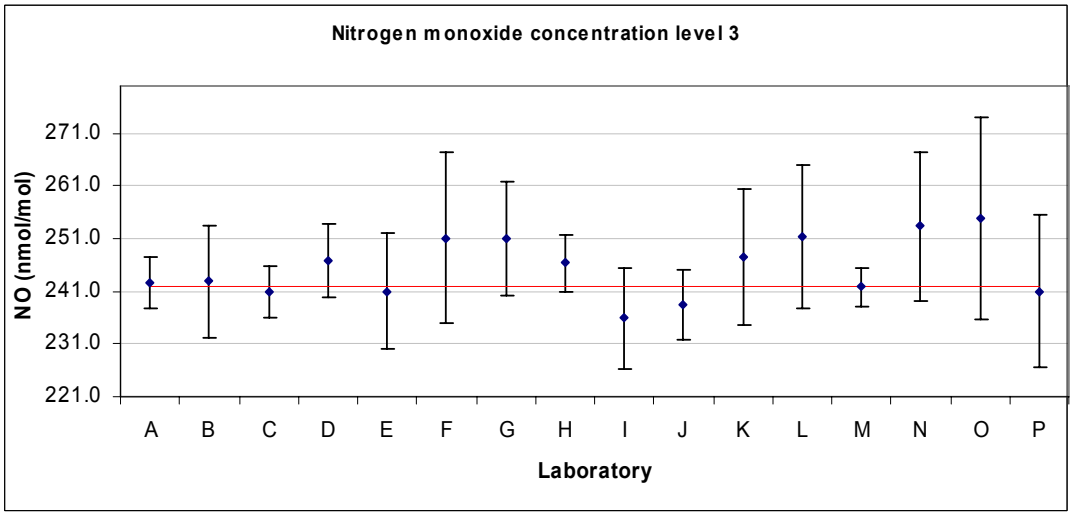

Figure 33: Reported values for NO concentration level 3.

Table 29: Reported values for NO concentration level 4.

parameter: NO level: 4 all units are nmol/mol x*: 144.24 s*: 2.67

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	143.4	142.44	143.0	145.9	144.13	147.97	147.8	144.43	137.93	143.40	146.55	148.79	142.69	143.45	149.35	137.02
xi,2	143.0	142.08	142.6	145.8	144.14	147.73	147.5	144.00	137.70	142.80	146.21	148.66	142.40	140.34	149.16	137.15
xi,3	142.5	142.05	142.3	144.3	143.49	147.42	146.8	143.62	137.23	142.40	145.66	148.29	141.77	144.71	149.08	136.06
xi	142.97	142.190	142.63	145.33	143.920	147.707	147.37	144.017	137.620	142.867	146.140	148.580	142.287	142.833	149.197	136.743
si	0.45	0.217	0.35	0.90	0.372	0.276	0.51	0.405	0.357	0.503	0.449	0.259	0.470	2.249	0.139	0.595
u(xi)	1.5	3.16	1.50	2.263	3.43	4.73	3.3	1.57	2.82	2.00	4	4.61	1.24	1.59	5.59	4.14
U(xi)	2.9	6.31	3.00	4.527	6.72	9.47	6.9	3.20	5.64	4.00	7	9.21	2.49	5.05	11.19	8.28

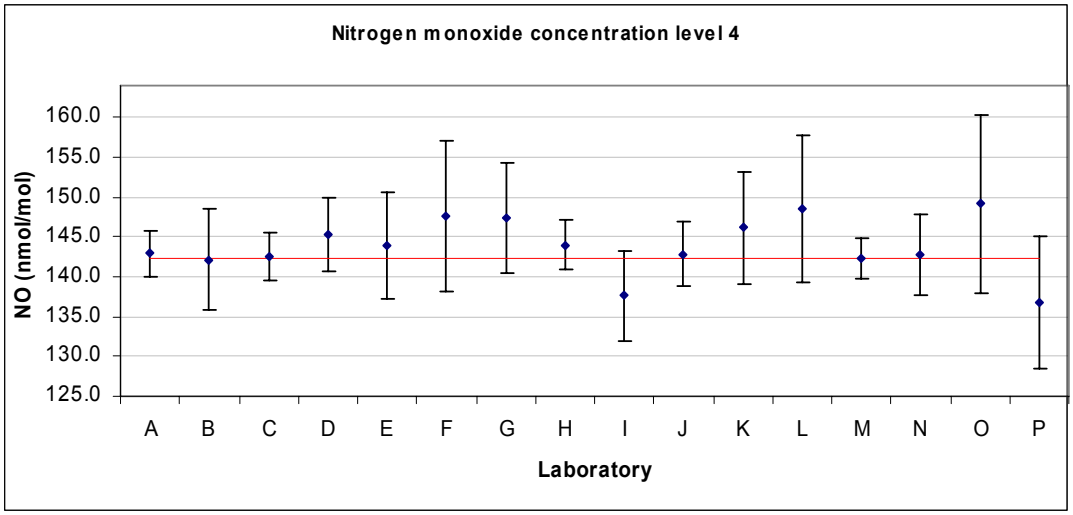

Figure 34: Reported values for NO concentration level 4.

Table 30: Reported values for NO concentration level 5.

parameter: NO level: 5 all units are nmol/mol x*: 146.56 s*: 2.47

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	145.9	144.97	145.4	147.2	144.46	151.53	151.1	147.32	140.44	144.10	147.95	152.06	145.54	141.30	152.86	144.32
xi,2	146.0	145.03	145.5	146.8	144.83	151.58	151.1	147.58	140.49	144.20	148.35	152.05	145.77	139.64	153.03	144.92
xi,3	146.1	145.14	145.5	148.6	144.64	151.57	151.1	147.71	140.48	144.00	148.28	152.41	145.80	138.76	153.12	144.61
xi	146.00	145.047	145.47	147.53	144.643	151.560	151.10	147.537	140.470	144.100	148.193	152.173	145.703	139.900	153.003	144.617
si	0.10	0.086	0.06	0.95	0.185	0.026	0.00	0.199	0.026	0.100	0.214	0.205	0.142	1.290	0.132	0.300
u(xi)	1.5	3.09	1.45	2.289	3.45	4.86	3.2	1.61	2.88	2.02	4	4.68	1.08	3.29	5.74	4.34
U(xi)	2.9	6.19	2.90	4.579	6.76	9.71	6.5	3.30	5.76	4.04	8	9.37	2.16	6.77	11.48	8.69

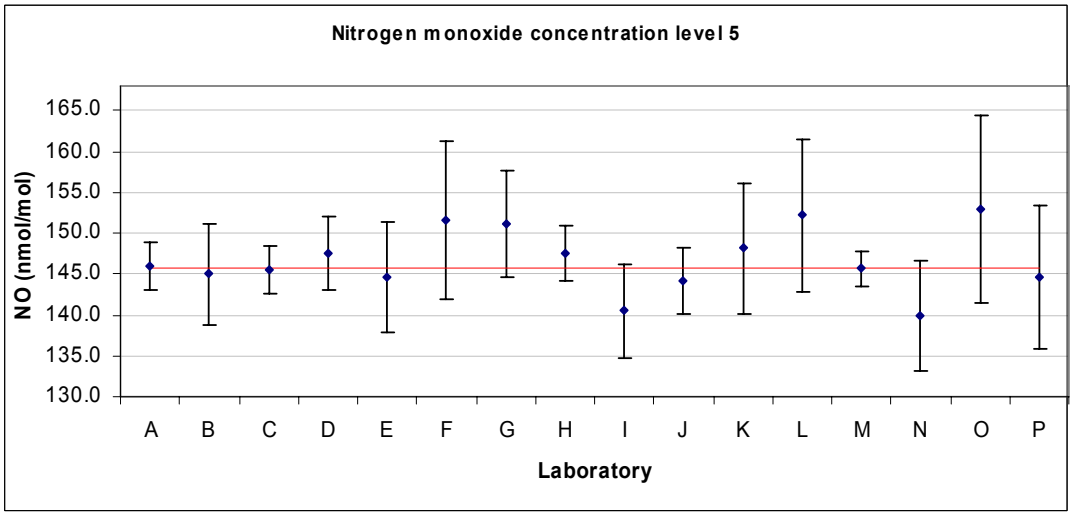

Figure 35: Reported values for NO concentration level 5.

Table 31: Reported values for NO concentration level 6.

parameter: NO	level: 6	all units are nmol/mol	x*: 89.10	s*: 1.26

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	88.4	87.43	88.6	88.55	88.84	91.65	91.3	89.09	84.46	88.60	90.33	92.48	88.28	89.94	92.27	84.72
xi,2	88.4	87.38	88.6	90.04	89.13	91.71	91.4	88.94	84.47	88.60	90.37	92.61	88.31	93.89	92.50	84.83
xi,3	88.4	87.42	88.6	89.77	89.03	91.75	91.5	88.98	84.41	88.60	90.35	92.59	88.34	94.65	92.44	84.74
xi	88.40	87.410	88.60	89.453	89.000	91.703	91.40	89.003	84.447	88.600	90.350	92.560	88.310	92.827	92.403	84.763
si	0.00	0.026	0.00	0.794	0.147	0.050	0.10	0.078	0.032	0.000	0.020	0.070	0.030	2.529	0.119	0.059
u(xi)	0.9	1.92	0.88	1.595	2.26	2.94	2.2	1.06	1.73	1.17	2	3.40	0.70	1.8	3.47	3.39
U(xi)	1.8	3.84	1.76	3.190	4.43	5.88	4.4	2.20	3.46	2.34	5	6.79	1.40	4.15	6.93	6.79

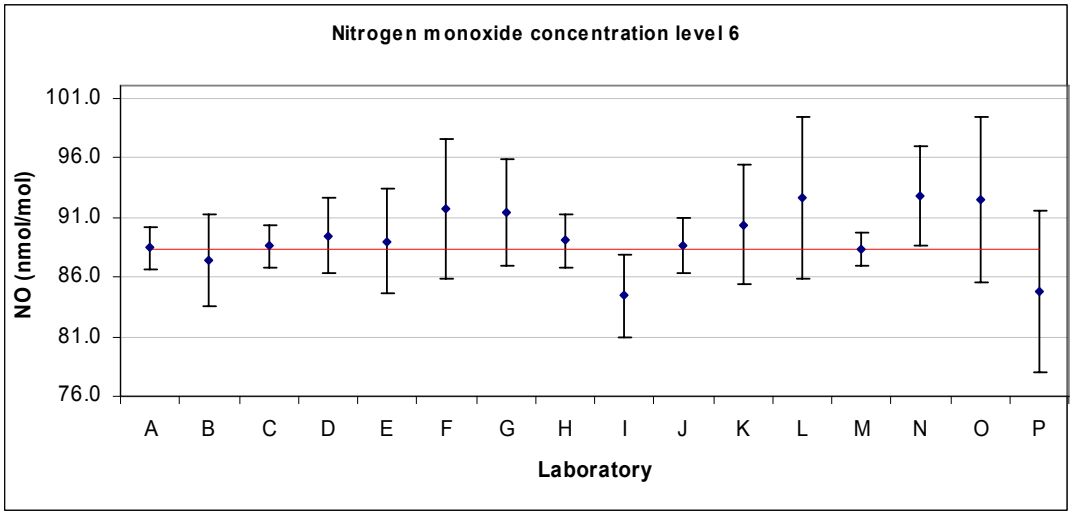

Figure 36: Reported values for NO concentration level 6.

Table 32: Reported values for NO concentration level 7.

parameter: NO	level: 7	all units are nmol/mol	x*: 48.96	s*: 1.31

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	48.4	47.68	48.5	49.77	47.83	50.50	50.5	48.54	46.00	47.80	48.90	50.97	49.07	49.94	50.92	47.40
xi,2	48.6	47.90	48.6	49.63	48.21	50.69	50.6	48.85	46.04	47.90	48.92	51.10	49.18	46.58	51.03	47.82
xi,3	48.7	47.92	48.8	49.50	48.34	50.67	50.6	49.02	45.97	48.00	49.19	51.16	49.23	52.90	51.05	48.11
xi	48.57	47.833	48.63	49.633	48.127	50.620	50.57	48.803	46.003	47.900	49.003	51.077	49.160	49.807	51.000	47.777
si	0.15	0.133	0.15	0.135	0.265	0.104	0.06	0.243	0.035	0.100	0.162	0.097	0.082	3.162	0.070	0.357
u(xi)	0.5	1.10	0.52	1.118	1.48	1.62	1.3	0.80	0.95	0.67	1	2.50	0.48	3.16	1.91	1.46
U(xi)	1.0	2.20	1.03	2.237	2.91	3.24	2.6	1.60	1.89	1.34	2	5.00	0.96	7.85	3.83	2.93

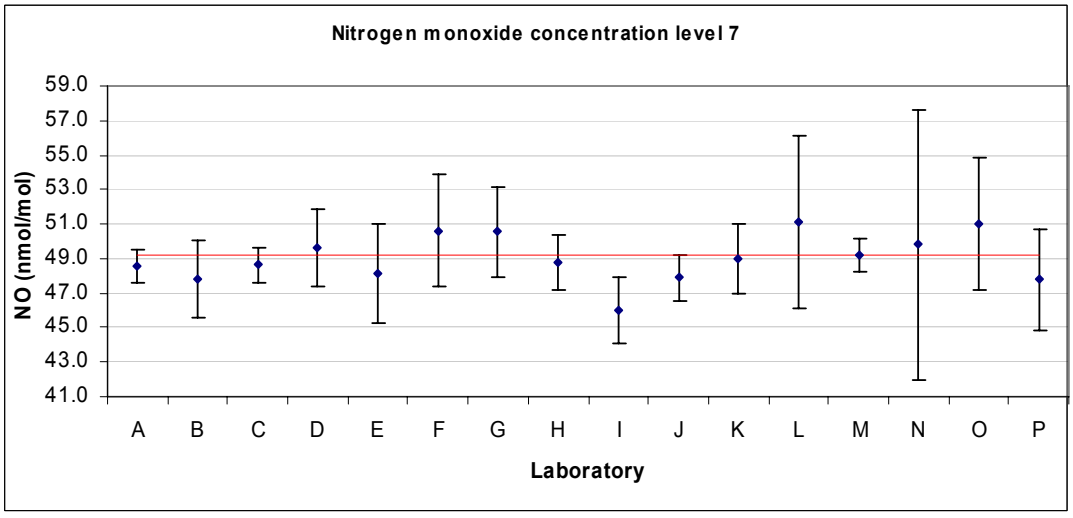

Figure 37: Reported values for NO concentration level 7.

Table 33: Reported values for NO concentration level 8.

parameter: NO level: 8 all units are nmol/mol x*: 28.43 s*: 0.41

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	28.4	27.51	28.4	29.45	28.46	29.16	29.3	28.15	26.08	28.20	28.46	29.78	28.47	23.04	29.54	26.45
xi,2	28.4	27.47	28.3	29.06	28.52	29.16	29.3	28.14	26.04	28.30	28.37	29.73	28.42	25.32	29.52	26.35
xi,3	28.3	27.49	28.4	29.47	28.55	29.14	29.3	28.14	26.05	28.00	28.27	29.76	28.47	27.49	29.51	25.01
xi	28.37	27.490	28.37	29.327	28.510	29.153	29.30	28.143	26.057	28.167	28.367	29.757	28.453	25.283	29.523	25.937
si	0.06	0.020	0.06	0.231	0.046	0.012	0.00	0.006	0.021	0.153	0.095	0.025	0.029	2.225	0.015	0.804
u(xi)	0.3	0.70	0.31	0.875	1.19	0.93	1.0	0.73	0.54	1.09	0.7	2.04	0.38	2.22	1.11	1.00
U(xi)	0.6	1.40	0.62	1.751	2.34	1.87	2.0	1.50	1.07	2.18	1	4.07	0.76	5.52	2.21	2.01

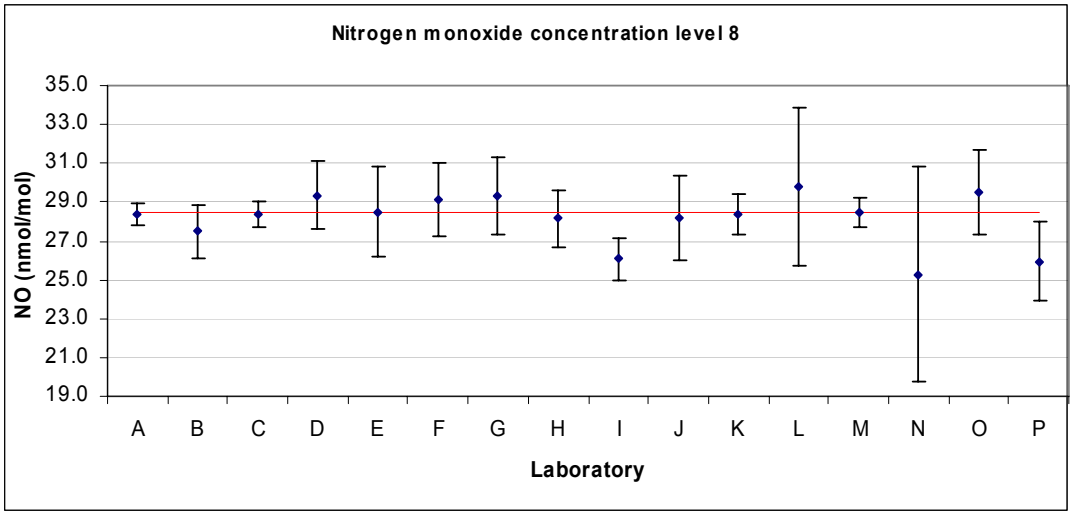

Figure 38: Reported values for NO concentration level 8.

Table 34: Reported values for NO concentration level 9.

parameter: NO level: 9 all units are nmol/mol x*: 14.70 s*: 0.56

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	14.8	14.12	14.9	15.58	14.40	15.13	15.4	14.50	13.44	14.70	14.59	15.57	14.78	13.06	15.45	13.90
xi,2	14.8	14.02	14.7	15.76	14.34	14.98	15.3	14.29	13.44	14.40	14.40	15.51	14.67	11.63	15.32	14.20
xi,3	14.7	14.02	14.7	15.78	14.30	14.92	15.2	14.19	13.38	14.50	14.48	15.42	14.61	13.54	15.24	13.22
xi	14.77	14.053	14.77	15.707	14.347	15.010	15.30	14.327	13.420	14.533	14.490	15.500	14.687	12.743	15.337	13.773
si	0.06	0.058	0.12	0.110	0.050	0.108	0.10	0.158	0.035	0.153	0.095	0.075	0.086	0.994	0.106	0.502
u(xi)	0.3	0.48	0.21	0.713	1.05	0.48	0.9	0.73	0.28	0.71	0.5	1.73	0.33	0.99	0.77	0.56
U(xi)	0.6	0.96	0.42	1.425	2.06	0.96	1.8	1.50	0.55	1.42	1	3.45	0.67	2.72	1.53	1.13

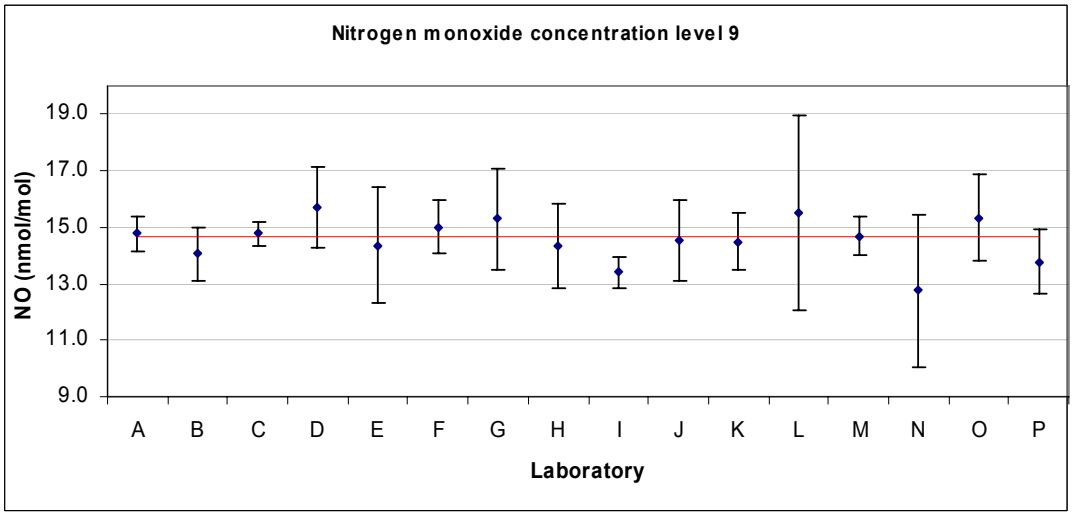

Figure 39: Reported values for NO concentration level 9.

Table 35: Reported values for NO concentration level 10.

parameter: NO	level: 10	all units are nmol/mol	x*: 2.68	s*: 0.35

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	2.8	2.15	2.8	3.784	2.80	2.32	2.7	2.30	1.79	2.70	2.48	3.01	2.68	2.87	2.80	2.31
xi,2	2.8	2.10	2.7	3.688	2.64	2.31	2.6	2.30	1.80	2.70	2.46	3.00	2.71	1.18	2.81	1.81
xi,3	2.8	2.42	3.0	4.049	3.08	2.65	3.1	2.55	1.86	2.60	2.69	3.34	3.05	1.85	3.18	2.05
xi	2.80	2.223	2.83	3.8403	2.840	2.427	2.80	2.383	1.817	2.667	2.543	3.117	2.813	1.967	2.930	2.057
si	0.00	0.172	0.15	0.1870	0.223	0.193	0.26	0.144	0.038	0.058	0.127	0.193	0.206	0.851	0.217	0.250
u(xi)	0.3	0.37	0.12	0.571	1.00	0.08	0.8	0.75	0.04	1.38	0.5	1.50	0.35	1.15	0.73	0.19
U(xi)	0.5	0.75	0.23	1.141	1.96	0.16	1.6	1.60	0.07	2.76	1	3.00	0.71	2.87	1.47	0.39

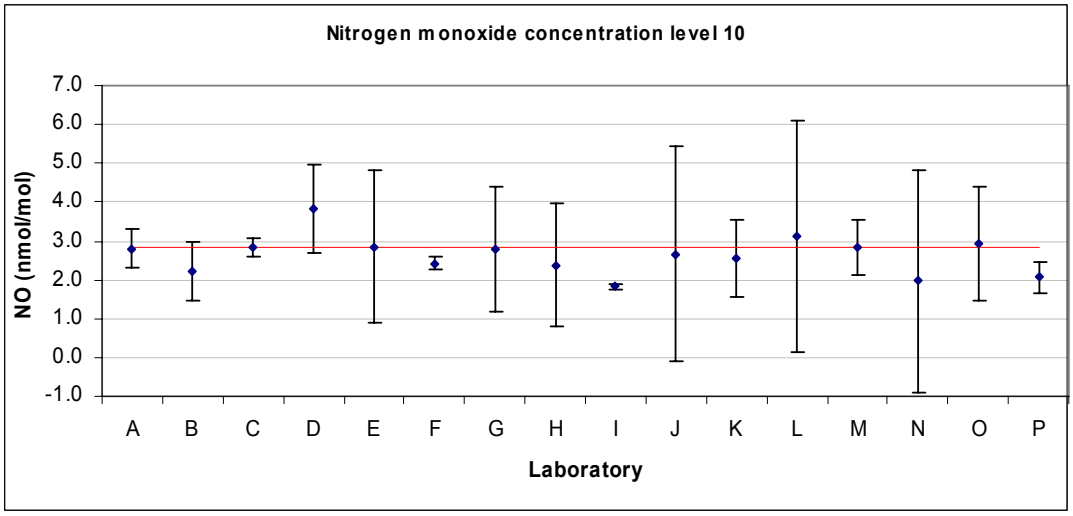

Figure 40: Reported values for NO concentration level 10.

Reported values for NO_2

Table 36: Reported values for NO_2 concentration level 0.

parameter: NO2	level: 0	all units are nmol/mol	x*: 0.01	s*: 0.36

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	-0.3	-0.17	0.3	0.347	0.28	0.06	-0.2	0.45	0.01	-0.70	-0.94	0.04	0.27	-0.07	-0.25	-4.32
u(xi)	0.4	0.52	0.10	0.529	1.00	0.00	1.0	0.87	0.00	0.75	0.5	1.50	0.90	0.22	1.00	0.13
U(xi)	0.7	1.05	0.20	1.058	1.96	0.01	2.0	1.80	0.00	1.50	1	3.00	1.79	0.45	2.00	0.26

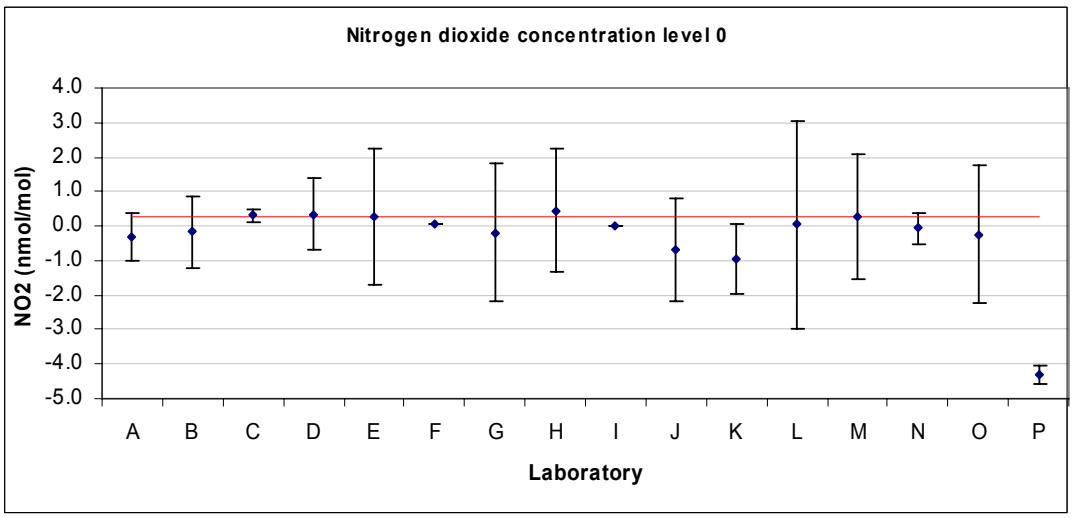

Figure 41: Reported values for NO_2 concentration level 0.

Table 37: Reported values for NO_2 concentration level 1.

parameter: NO2	level: 1	all units are nmol/mol								x*: 4.32		s*: 1.18		
	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	5.7	4.90	3.9	0.218	5.52	7.79	2.6	6.24	6.78	7.50	5.38	5.39	5.21	0.56
xi,2	4.5	3.79	2.3	-0.501	4.51	6.32	1.7	4.28	5.25	7.00	3.02	4.07	3.92	-0.91
xi,3	4.1	3.29	2.2	-1.861	3.56	5.68	1.2	3.15	5.00	7.00	2.80	3.70	3.10	-1.67
xi	4.77	3.993	2.80	-0.7147	4.530	6.597	1.83	4.557	5.677	7.167	3.733	4.387	4.077	-0.673
si	0.83	0.824	0.95	1.0558	0.980	1.082	0.71	1.563	0.964	0.289	1.430	0.888	1.064	1.134
u(xi)	0.4	0.61	0.04	0.516	1.01	0.31	1.0	0.85	0.12	0.36	0.5	1.50	1.65	1.00
U(xi)	0.8	1.22	0.08	1.032	1.97	0.63	2.0	1.80	0.23	0.72	1	3.00	3.30	2.00

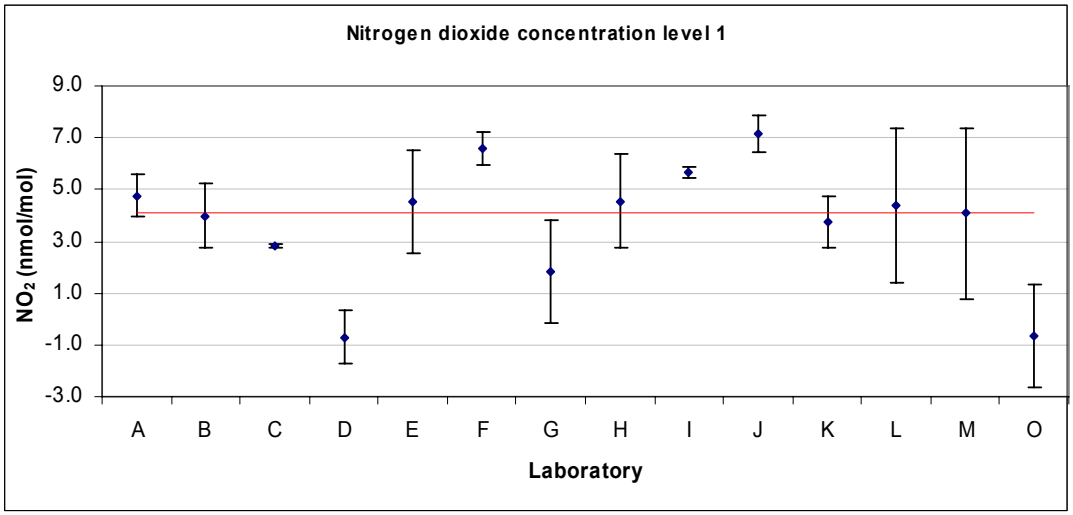

Figure 42: Reported values for NO_2 concentration level 1.

Table 38: Reported values for NO_2 concentration level 2.

parameter: NO2	level: 2	all units are nmol/mol									x*: 119.45		s*: 3.50				
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	
xi,1	120.1	121.99	117.6	115.5	115.19	127.06	118.6	123.98	116.22	118.90	118.61	122.66	119.73	122.54	122.18	112.51	
xi,2	120.1	121.84	115.9	115.4	115.57	126.94	118.7	123.79	117.12	119.00	118.20	122.53	119.58	113.13	122.18	113.12	
xi,3	120.1	122.47	115.7	115.7	115.11	126.97	118.8	123.82	116.86	118.90	118.41	122.59	119.75	111.11	122.13	114.25	
xi	120.10	122.100	116.40	115.53	115.290	126.990	118.70	123.863	116.733	118.933	118.407	122.593	119.687	115.593	122.163	113.293	
si	0.00	0.329	1.04	0.15	0.246	0.062	0.10	0.102	0.463	0.058	0.205	0.065	0.093	6.100	0.029	0.883	
u(xi)	1.2	4.49	1.88	1.907	2.81	5.94	2.9	1.40	2.40	1.66	3	4.05	2.38	3.52	5.19	3.43	
U(xi)	2.4	8.99	3.75	3.814	5.51	11.88	5.8	2.90	4.79	3.33	6	8.09	4.76	7.55	10.38	6.86	

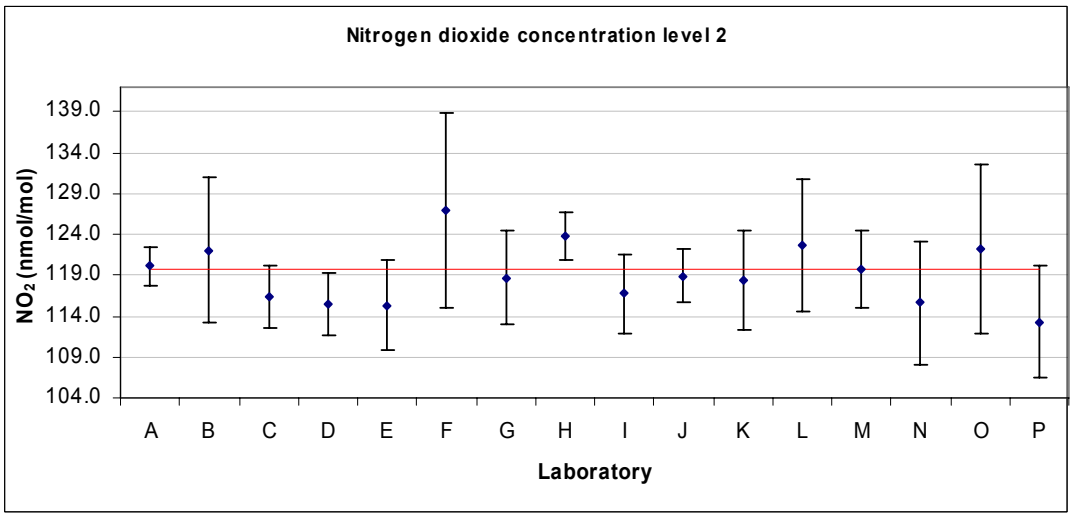

Figure 43: Reported values for NO_2 concentration level 2.

Table 39: Reported values for NO_2 concentration level 3.

parameter: NO2	level: 3	all units are nmol/mol	x*: 1.92	s*: 1.06

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	2.2	1.70	1.2	1.885	2.62	3.50	0.4	2.76	2.84	3.60	1.56	2.33	2.44	0.03
xi,2	2.0	1.03	1.0	0.610	1.88	3.28	0.3	2.22	2.68	3.60	1.23	2.19	2.08	-0.28
xi,3	1.9	0.95	0.9	0.398	1.80	3.10	0.2	2.13	2.28	3.30	0.79	2.14	1.86	-0.36
xi	2.03	1.227	1.03	0.9643	2.100	3.293	0.30	2.370	2.600	3.500	1.193	2.220	2.127	-0.203
si	0.15	0.412	0.15	0.8043	0.452	0.200	0.10	0.341	0.288	0.173	0.386	0.098	0.293	0.206
u(xi)	0.4	0.54	0.32	0.536	1.00	0.16	1.0	0.86	0.06	0.36	0.5	1.50	0.99	1.00
U(xi)	0.7	1.09	0.63	1.072	1.96	0.31	2.0	1.80	0.11	0.72	1	3.00	1.98	2.00

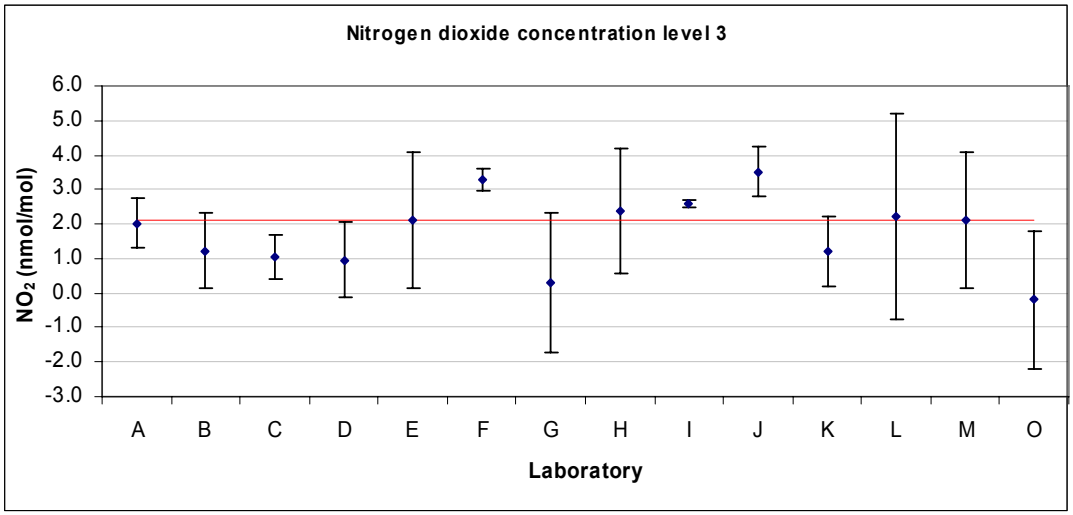

Figure 44: Reported values for NO_2 concentration level 3.

Table 40: Reported values for NO_2 concentration level 4.

parameter: NO2	level: 4	all units are nmol/mol	x*: 101.70	s*: 3.12

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	102.2	101.57	101.0	101.5	98.30	107.71	103.9	104.62	96.93	99.20	100.05	104.93	102.38	100.40	105.26	95.74
xi,2	102.2	101.49	100.7	101.9	98.05	107.70	103.5	104.83	97.18	99.20	99.94	104.94	102.44	102.79	105.25	95.82
xi,3	102.1	101.45	100.3	100.6	98.23	107.62	103.6	104.74	96.82	99.20	99.81	105.06	102.44	107.94	105.28	95.91
xi	102.17	101.503	100.67	101.33	98.193	107.677	103.67	104.730	96.977	99.200	99.933	104.977	102.420	103.710	105.263	95.823
si	0.06	0.061	0.35	0.67	0.129	0.049	0.21	0.105	0.184	0.000	0.120	0.072	0.035	3.853	0.015	0.085
u(xi)	1.4	2.78	1.08	1.737	2.45	5.04	2.4	1.23	1.99	1.39	3	3.67	1.62	3.85	4.47	2.89
U(xi)	2.7	5.56	2.16	3.473	4.81	10.07	4.8	2.50	3.98	2.78	5	7.33	3.25	9.57	8.95	5.78

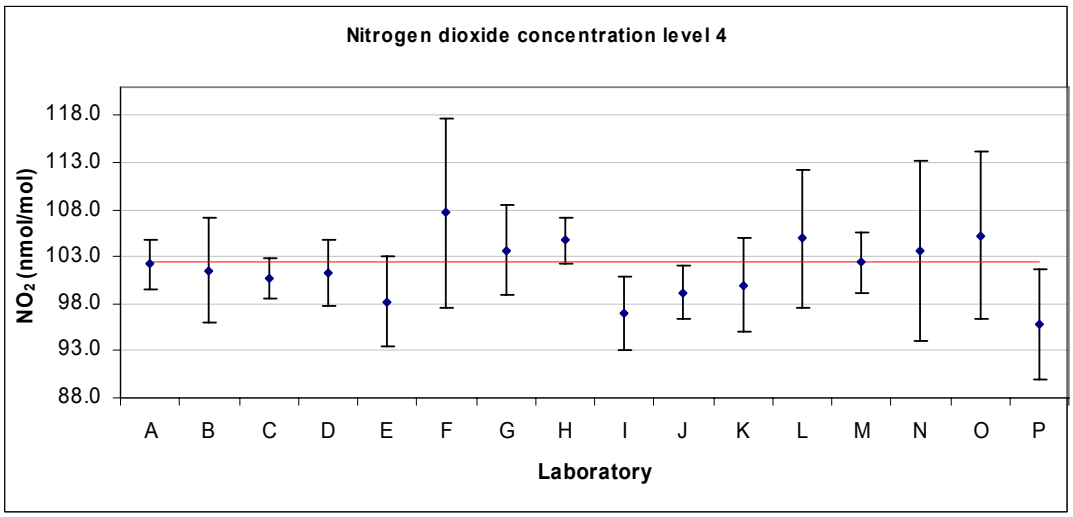

Figure 45: Reported values for NO_2 concentration level 4.

Table 41: Reported values for NO_2 concentration level 5.

parameter: NO2	level: 5	all units are nmol/mol	x*: 1.07	s*: 0.68

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	1.3	0.10	0.7	1.051	1.57	2.17	0.2	1.76	1.56	1.70	0.06	1.59	1.72	0.30
xi,2	1.2	-0.20	0.5	0.300	1.28	1.93	0.2	1.58	1.38	1.70	-0.03	1.37	1.22	-0.12
xi,3	1.1	-0.29	0.5	0.389	0.92	1.90	-0.1	1.54	1.30	1.70	0.17	1.11	1.07	-0.23
xi	1.20	-0.130	0.57	0.5800	1.257	2.000	0.10	1.627	1.413	1.700	0.067	1.357	1.337	-0.017
si	0.10	0.204	0.12	0.4103	0.326	0.148	0.17	0.117	0.133	0.000	0.100	0.240	0.340	0.280
u(xi)	0.4	0.53	0.21	0.532	1.00	0.09	1.0	0.86	0.03	0.75	0.5	1.50	0.48	1.00
U(xi)	0.7	1.06	0.42	1.063	1.96	0.19	2.0	1.80	0.06	1.50	1	3.00	0.97	2.00

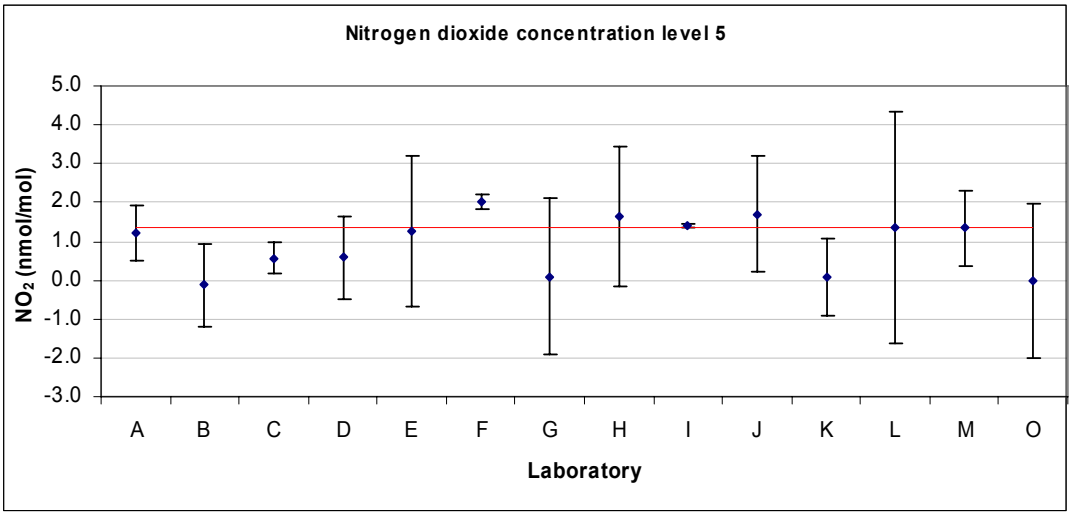

Figure 46: Reported values for NO_2 concentration level 5.

Table 42: Reported values for NO_2 concentration level 6.

parameter: NO2	level: 6	all units are nmol/mol	x*: 58.31	s*: 2.17

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	58.9	57.26	58.4	58.09	56.39	62.28	59.6	60.00	55.17	56.70	56.63	60.95	59.11	56.27	60.58	52.74
xi,2	58.9	57.20	58.2	58.35	55.97	62.13	59.5	60.00	55.11	56.90	56.28	60.73	59.11	59.28	60.36	52.75
xi,3	58.8	57.06	58.2	58.45	56.14	62.07	59.3	60.00	54.92	56.90	56.44	60.66	59.00	58.00	60.30	52.84
xi	58.87	57.173	58.27	58.297	56.167	62.160	59.47	60.000	55.067	56.833	56.450	60.780	59.073	57.850	60.413	52.777
si	0.06	0.103	0.12	0.186	0.211	0.108	0.15	0.000	0.131	0.115	0.175	0.151	0.064	1.511	0.147	0.055
u(xi)	1.0	1.66	0.51	1.228	1.62	2.91	1.6	0.92	1.13	0.79	1	2.71	0.81	1.68	2.57	1.50
U(xi)	1.9	3.32	1.02	2.455	3.18	5.81	3.2	1.90	2.26	1.58	3	5.42	1.63	3.55	5.14	3.01

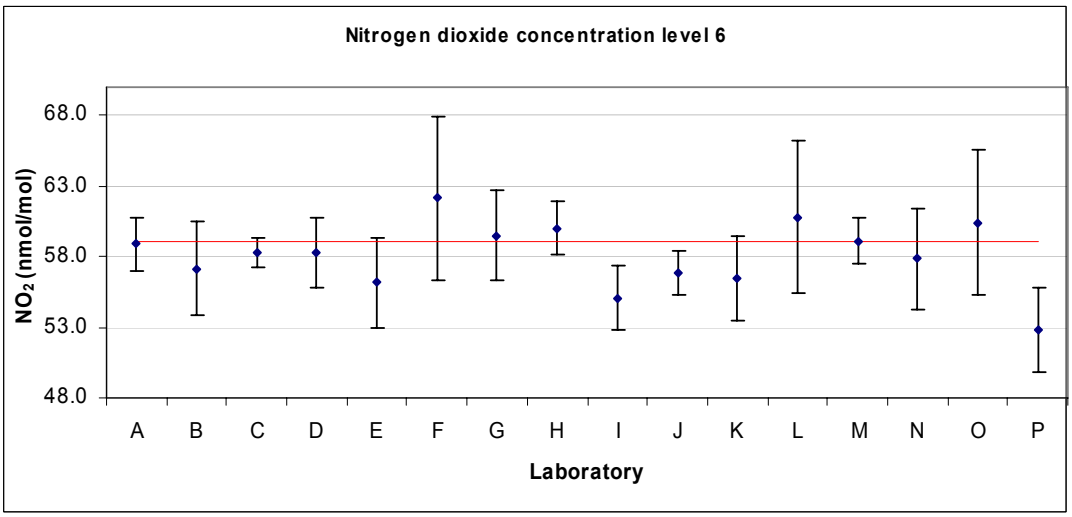

Figure 47: Reported values for NO_2 concentration level 6.

Table 43: Reported values for NO_2 concentration level 7.

parameter: NO2	level: 7	all units are nmol/mol	x*: 0.72	s*: 0.39

	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	0.7	-0.62	0.8	1.410	0.86	1.24	0.7	1.51	0.69	0.60	-0.69	1.06	1.07	0.89
xi,2	0.6	-0.89	0.7	1.117	0.62	1.02	0.5	1.29	0.63	0.30	-0.89	0.87	1.01	0.73
xi,3	0.5	-0.88	0.5	1.386	0.66	0.98	0.5	1.07	0.63	0.50	-0.81	0.77	0.84	0.61
xi	0.60	-0.797	0.67	1.3043	0.713	1.080	0.57	1.290	0.650	0.467	-0.797	0.900	0.973	0.743
si	0.10	0.153	0.15	0.1627	0.129	0.140	0.12	0.220	0.035	0.153	0.101	0.147	0.119	0.140
u(xi)	0.4	0.52	0.10	0.540	1.00	0.05	1.0	0.86	0.02	0.75	0.5	1.50	0.28	1.00
U(xi)	0.7	1.05	0.20	1.081	1.96	0.10	2.0	1.80	0.03	1.50	1	3.00	0.57	2.00

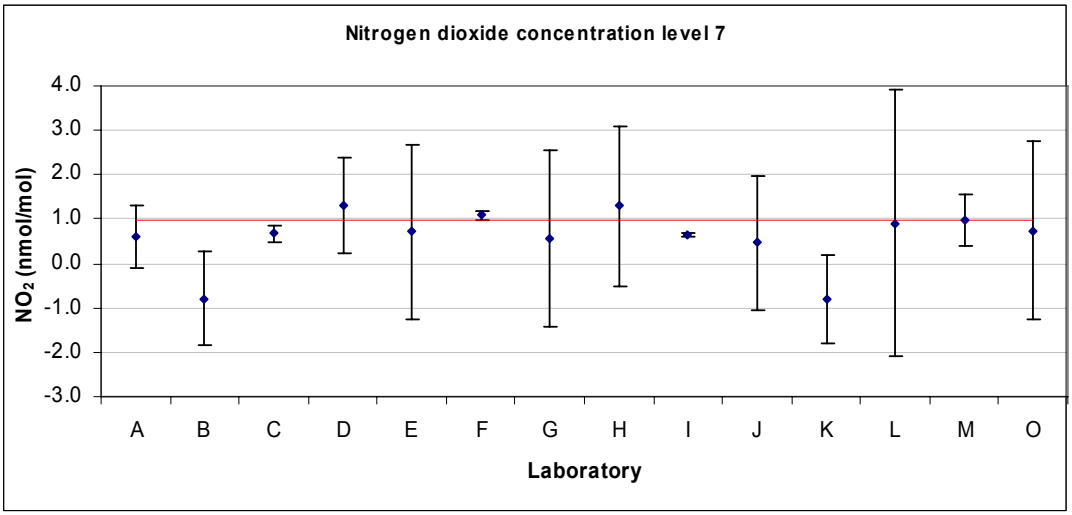

Figure 48: Reported values for NO_2 concentration level 7.

Table 44: Reported values for NO_2 concentration level 8.

parameter: NO2	level: 8	all units are nmol/mol	x*: 21.00	s*: 1.28

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
xi,1	21.1	19.51	21.2	21.84	20.33	22.74	21.9	21.91	19.58	19.80	19.52	22.08	21.74	21.49	22.00	18.25
xi,2	21.0	19.57	21.2	21.76	20.32	22.73	21.9	21.91	19.53	19.80	19.51	22.17	21.65	18.16	21.98	18.19
xi,3	21.0	19.57	21.2	21.92	20.23	22.68	21.8	21.72	19.48	20.00	19.34	22.05	21.61	20.31	21.88	18.22
xi	21.03	19.550	21.20	21.840	20.293	22.717	21.87	21.847	19.530	19.867	19.457	22.100	21.667	19.987	21.953	18.220
si	0.06	0.035	0.00	0.080	0.055	0.032	0.06	0.110	0.050	0.115	0.101	0.062	0.067	1.688	0.064	0.030
u(xi)	0.6	0.74	0.10	0.786	1.10	1.06	1.2	0.82	0.40	0.45	0.5	1.87	0.38	2.33	0.93	0.78
U(xi)	1.1	1.49	0.20	1.572	2.16	2.12	2.4	1.70	0.80	0.90	1	3.74	0.76	4.75	1.87	1.56

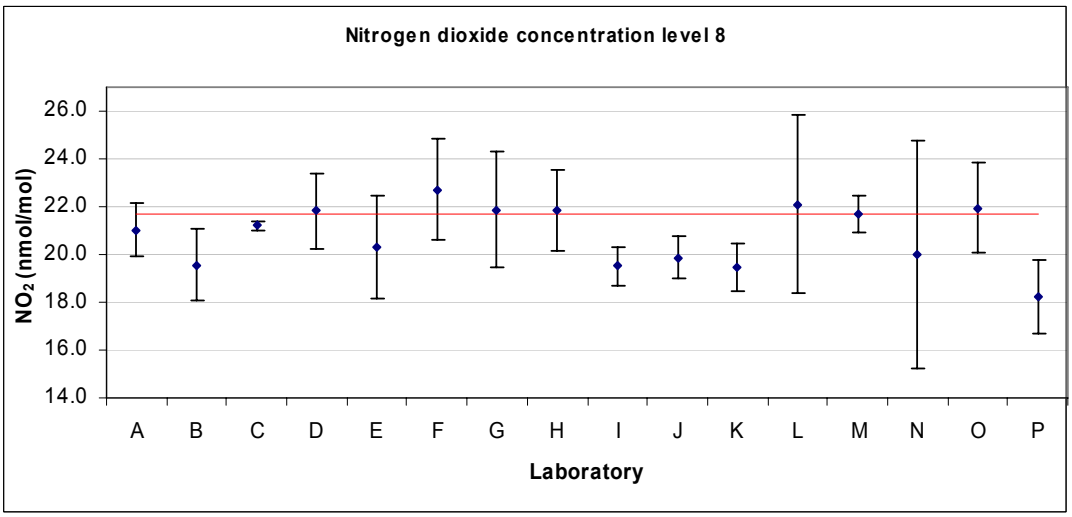

Figure 49: Reported values for NO_2 concentration level 8.

Table 45: Reported values for NO_2 concentration level 9.

parameter: NO2	level: 9	all units are nmol/mol								x*: 0.39		s*: 0.52		
	A	B	C	D	E	F	G	H	I	J	K	L	M	O
xi,1	0.1	-0.99	0.5	1.298	0.50	0.58	0.4	0.85	0.00	-0.10	-1.08	0.55	0.70	0.64
xi,2	0.2	-1.01	0.4	1.209	0.47	0.61	0.6	1.00	0.00	0.10	-1.00	0.53	0.78	0.66
xi,3	0.1	-0.95	0.5	1.502	0.55	0.65	0.6	0.98	0.03	0.00	-1.00	0.59	0.74	0.73
xi	0.13	-0.983	0.47	1.3363	0.507	0.613	0.53	0.943	0.010	0.000	-1.027	0.557	0.740	0.677
si	0.06	0.031	0.06	0.1502	0.040	0.035	0.12	0.081	0.017	0.100	0.046	0.031	0.040	0.047
u(xi)	0.4	0.52	0.10	0.541	1.00	0.03	1.0	0.86	0.00	0.75	0.5	1.50	0.16	1.00
U(xi)	0.7	1.05	0.20	1.081	1.96	0.06	2.0	1.80	0.00	1.50	1	3.00	0.32	2.00

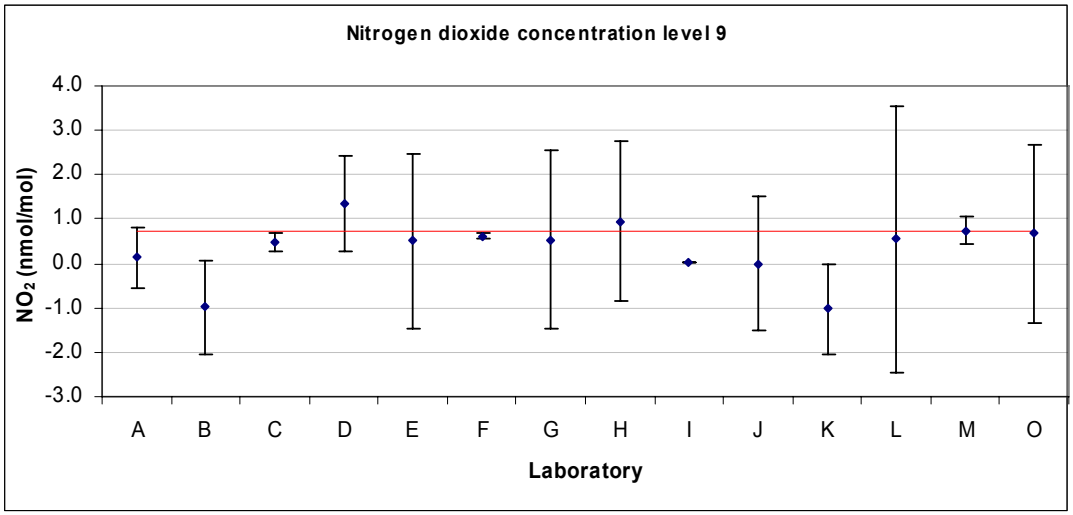

Figure 50: Reported values for NO_2 concentration level 9.

Table 46: Reported values for NO_2 concentration level 10.

parameter: NO2	level: 10	all units are nmol/mol									x*: 12.34		s*: 0.91				
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	
xi,1	12.2	10.77	12.5	13.39	11.98	13.28	12.9	12.92	11.25	11.40	10.55	12.88	12.78	18.16	13.06	11.22	
xi,2	12.1	10.83	12.5	13.58	11.97	13.28	13.0	12.94	11.19	11.40	10.51	12.95	12.79	18.99	13.03	12.08	
xi,3	12.2	10.92	12.5	13.65	11.99	13.24	13.0	12.92	11.13	11.30	10.47	12.89	12.80	16.71	13.09	11.52	
xi	12.17	10.840	12.50	13.540	11.980	13.267	12.97	12.927	11.190	11.367	10.510	12.907	12.790	17.953	13.060	11.607	
si	0.06	0.075	0.00	0.135	0.010	0.023	0.06	0.012	0.060	0.058	0.040	0.038	0.010	1.154	0.030	0.437	
u(xi)	0.6	0.58	0.13	0.687	1.04	0.62	1.0	0.83	0.23	0.39	0.5	1.67	0.31	0.85	0.98	0.64	
U(xi)	1.1	1.16	0.26	1.373	2.03	1.24	2.0	1.70	0.46	0.78	1	3.34	0.62	2.11	1.96	1.28	

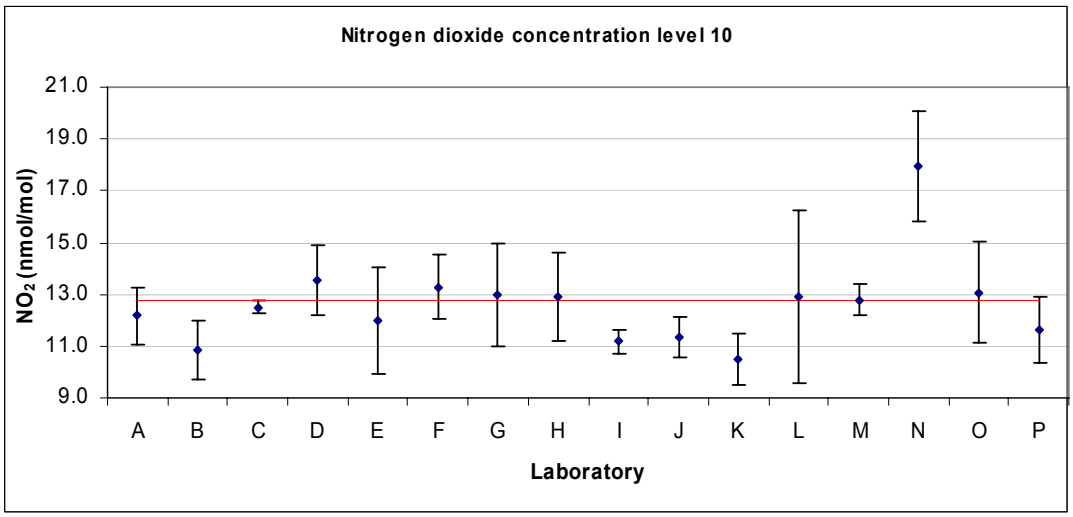

Figure 51: Reported values for NO_2 concentration level 10.

Annex C. Precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [6], [7], [8] and [9] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [18], [19] and [20]. The precision experiment involved thirteen laboratories. For O_3 four, CO and SO_2 five, NO ten, and NO_2 eleven concentration levels were tested. Data consistency and outlier tests have been performed (Annex D).

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using equation 8 [20]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,20} \cdot \sqrt{2} \cdot s_r \qquad (8)$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using equation 9 [20]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, that should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,9} \cdot \sqrt{2} \cdot s_R \qquad (9)$$

The repeatability standard deviation was evaluated with 26 (13·(3-1)) degrees of freedom (ν) and reproducibility standard deviation with 12 (13-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are 2,056 and 2,179 respectively.

In Table 47-Table 51 and Figure 52-Figure 58 the repeatability and reproducibility limits of measurement methods are presented with (r, R) and without (r*, R*) outliers. Also presented is 'reproducibility from common criteria (R(from σ_p))' calculated by substituting s_R in equation 9 with a 'standard deviation for proficiency assessment' (Table 3). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([17] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is fit for σ_p.

Table 47: The R and r of CO standard measurement method.

CO data (µmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.44		0.74	0.50		0.66	
1.43	0.06	0.53	1.48	0.06	0.44	
2.47	0.05	0.56	2.52	0.05	0.43	
4.62	0.08	0.54	4.67	0.07	0.35	
6.19	0.06	0.56	6.23	0.06	0.37	
8.35	0.03	0.64	8.39	0.04	0.45	5.4%

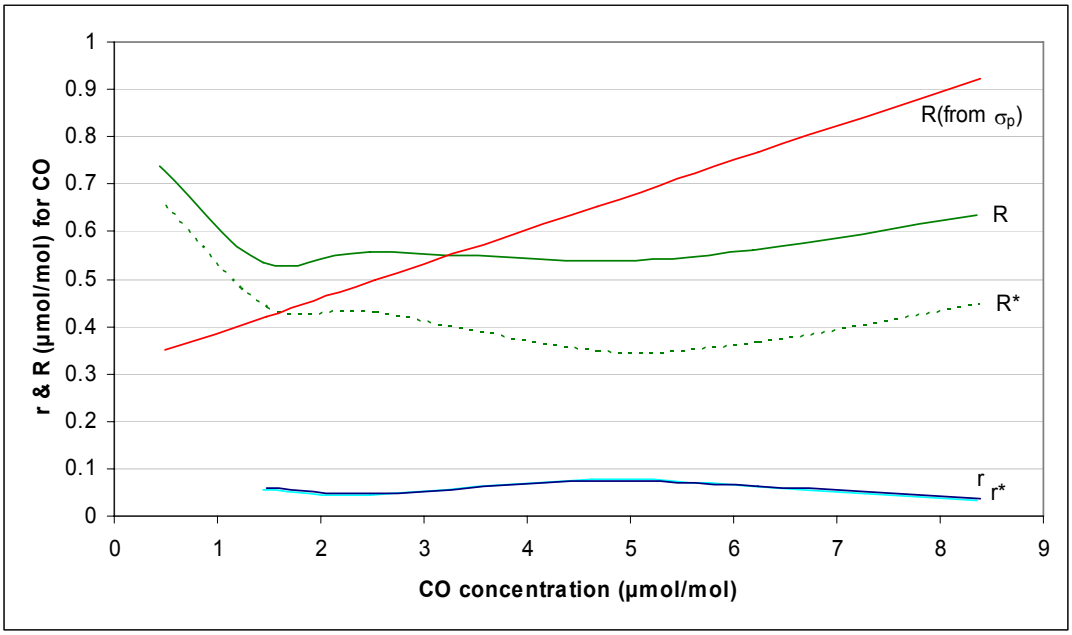

Figure 52: The R and r of CO standard measurement method as a function of concentration.

Table 48: The R and r of O_3 standard measurement method.

O3 data (nmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.3		1.2	0.2		1.3	
14.0	0.3	1.5	14.0	0.2	1.4	
57.5	1.2	3.1	57.3	1.2	2.2	
99.2	1.0	4.1	98.9	0.7	2.6	
113.9	2.7	3.3	113.9	2.1	3.1	2.7%

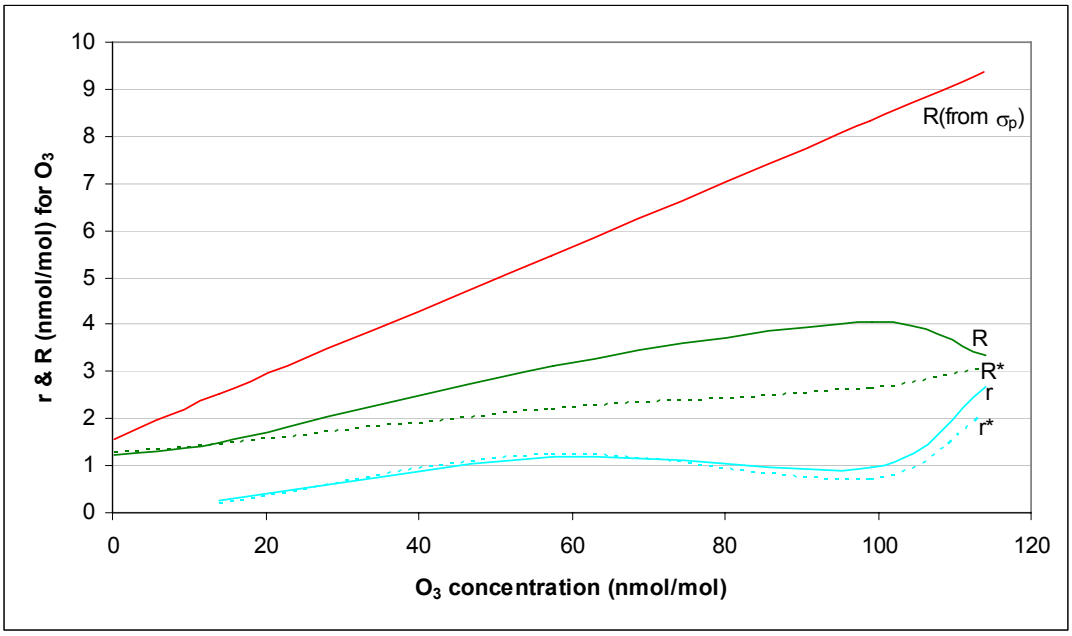

Figure 53: The R and r of O_3 standard measurement method as a function of concentration.

Table 49: The R and r of SO_2 standard measurement method.

SO2 data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3		1.6	
2.8	0.2	1.9	
6.9	0.3	1.6	
17.2	0.3	1.7	
44.5	0.4	3.3	
122.2	0.5	8.9	7.3%

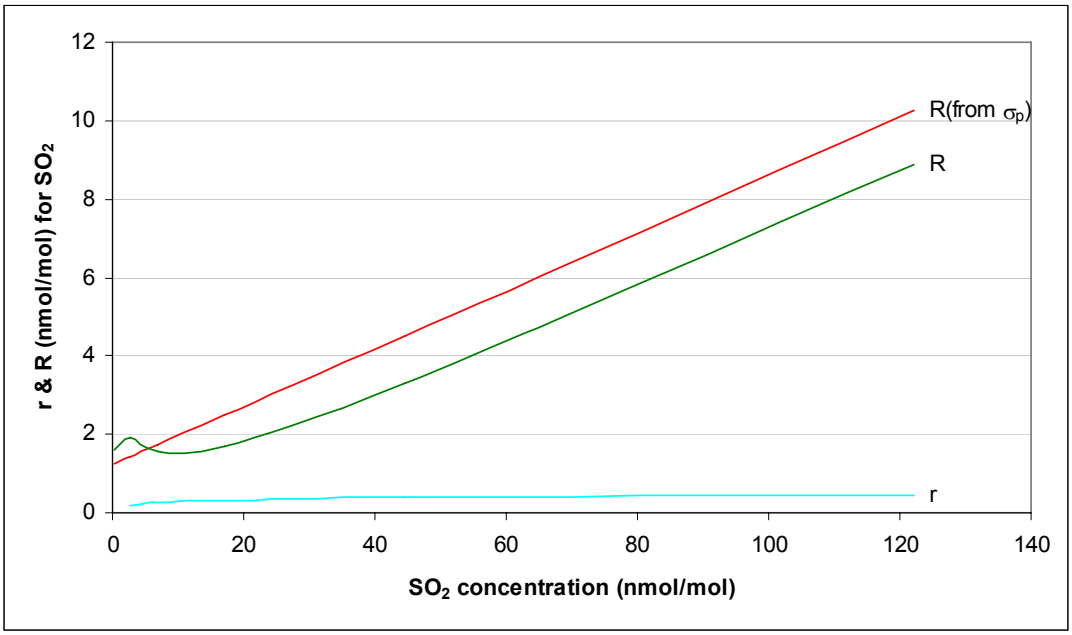

Figure 54: The R and r of SO_2 standard measurement method as a function of concentration.

Table 50: The R and r of NO standard measurement method.

NO data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
2.7	0.5	1.5	
3.4		0.9	
14.7	0.3	1.9	
28.4	0.3	2.9	
48.9	0.4	4.2	
89.2	0.7	6.4	
144.1	1.3	9.1	
146.9	0.8	10.2	
244.5	2.1	15.5	
490.8	1.8	26.2	5.3%

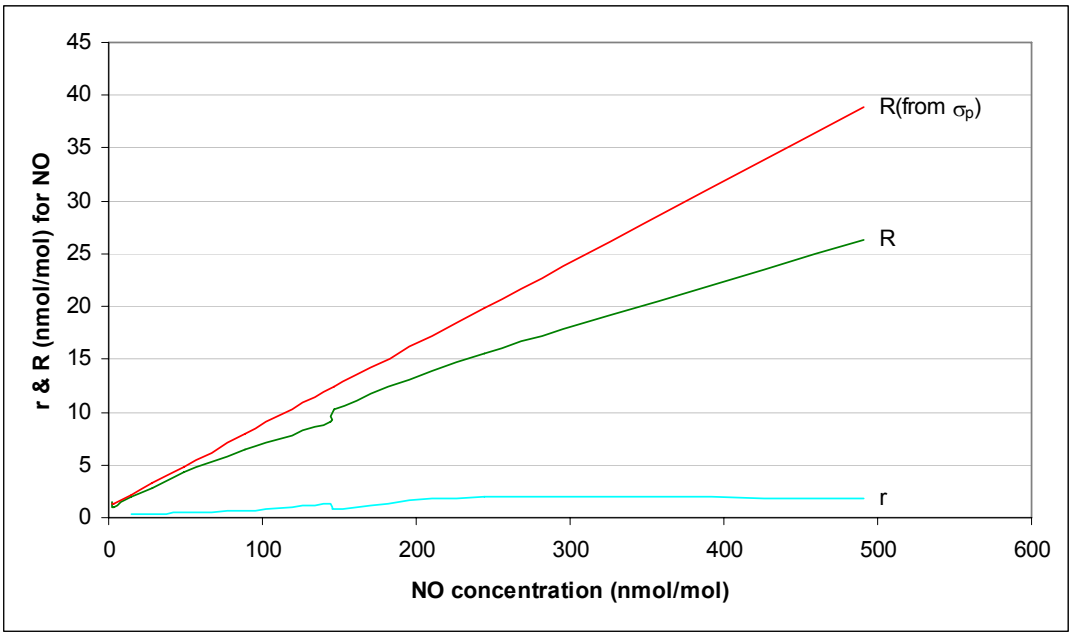

Figure 55: The R and r of NO standard measurement method as a function of concentration.

The reproducibility and repeatability of NO_2 measurements are dependant on both NO and NO_2 concentrations. In the following table both concentrations are given and in Figure 56 R is presented as a surface. In Figure 57 and Figure 58 projections of this surface are given.

Table 51: The R and r of NO_2 standard measurement method.

NO2 data (nmol/mol)				
all data				
NO	NO2	NO2		
group average	group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
3.4	0.0		1.3	
2.7	12.2	0.2	3.0	
14.7	0.3	0.2	2.1	
28.4	21.0	0.2	3.5	
48.9	0.6	0.4	2.1	
89.2	58.4	0.4	6.2	
146.9	1.0	0.6	2.2	
144.1	101.8	0.7	9.1	
244.5	1.9	1.0	3.0	
375.6	119.6	1.0	10.7	8.9%
490.8	4.1	3.0	6.7	

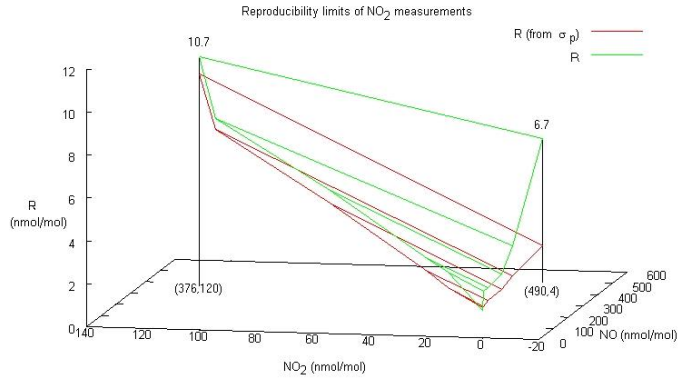

Figure 56: The R of NO_2 standard measurement method as a function of NO and NO_2 concentrations.

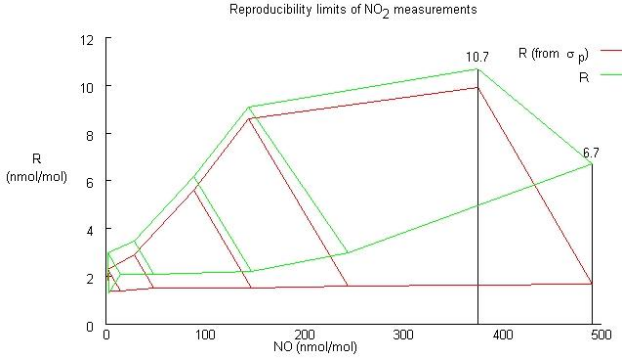

Figure 57: The projection of figure 57 to NO_2=0 plane.

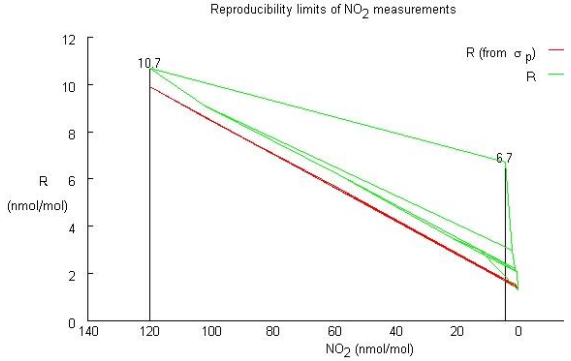

Figure 58: The projection of figure 57 to NO=0 plane.

Annex D. Scrutiny of results for consistency and outliers

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures. For that reason a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or calculation, the bad averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure the IE data first underwent the scrutiny for its consistency and the detection of statistical outliers as described in ISO 5725-2. Then the four laboratories showing some form of statistical inconsistency were contacted to try to ascertain the cause of discrepancies. Laboratories were allowed to correct their results and one did so. After that data was considered of appropriate quality and the final tests of statistical outliers were performed.
In this final test "Grubb's one outlying observation test" was performed Figure 59 to Figure 63. For runs:

a.) where outliers were detected outliers were removed and "Grubb's one outlying observation test" was repeated. After this one repetition there were no more outliers in these runs.
b.) where no outliers were detected the "Grubb's two outlying observations test" was performed (Figure 64 to Figure 68).

Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant's standard operating procedure. These "genuine" statistical outliers are presented in table below:

Table 52: "Genuine" statistical outliers.

Parameter	Run	Participant	Failing test
NO	2	all	See chapter 4
CO	1, 2, 3	J	"Grubb's one outlying observation test" (Figure 60)
O3	2, 3	J	"Grubb's one outlying observation test" (Figure 61)

Not to have unrealistic jumps in the evaluation of precision of standardized method all O_3 and SO_2 data of the participant J were removed from this evaluation. Even though it is not statistical outlier, the CO data of participant K was removed from evaluation, after it was discovered through exchange of information that not all requirements of IE were respected (participant did not use its own zero air for calibration of its instrument).

Presented in the following figures are Grubb's one outlying observation test statistics for the minimum (blue) and maximum (orange with pattern) values of each run. Values between the two lines are considered strugglers and values over violet line are considered outliers.

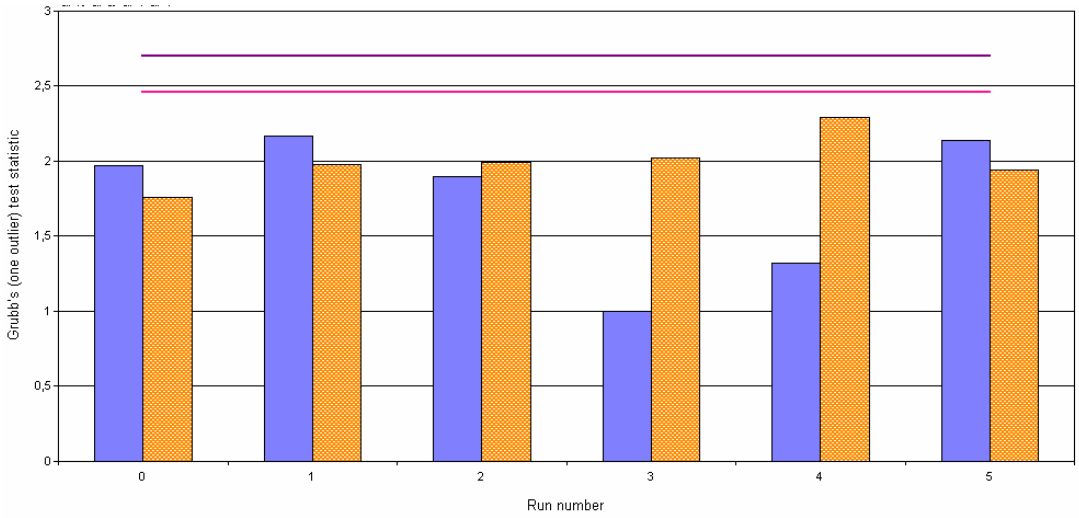

Figure 59: Grubb's one outlying observation test statistics for SO_2 runs.

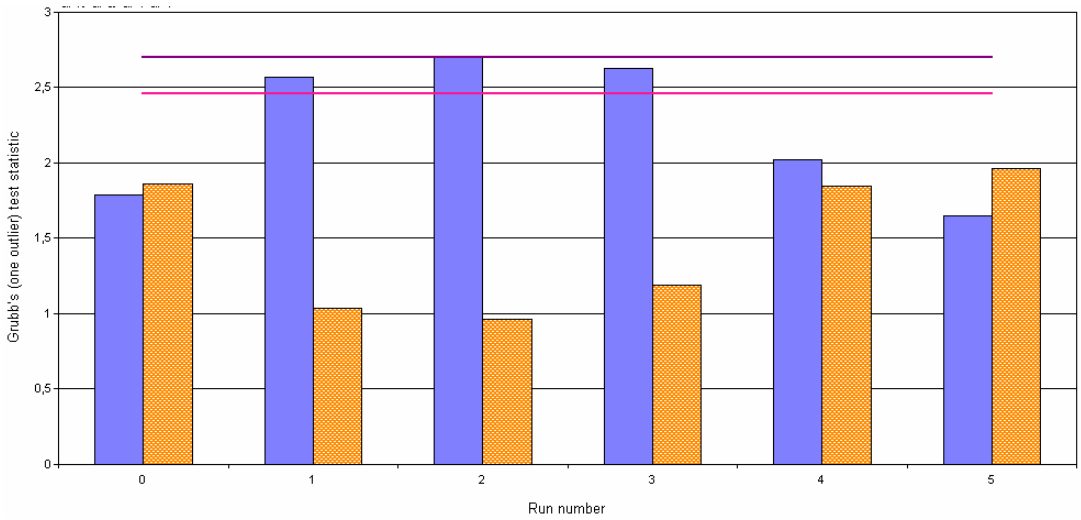

Figure 60: Grubb's one outlying observation test statistics for CO runs.

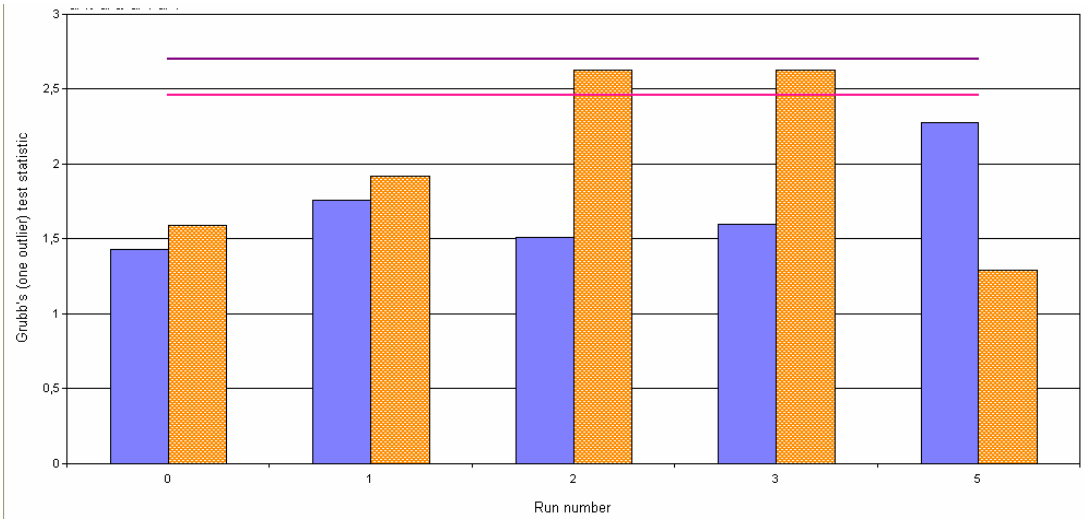

Figure 61: Grubb's one outlying observation test statistics for O_3 runs.

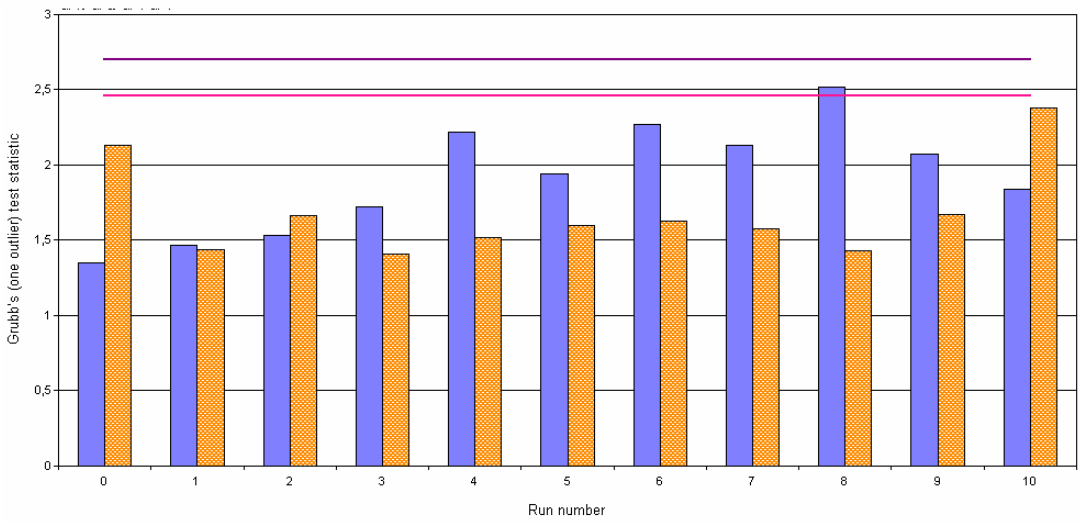

Figure 62: Grubb's one outlying observation test statistics for NO runs.

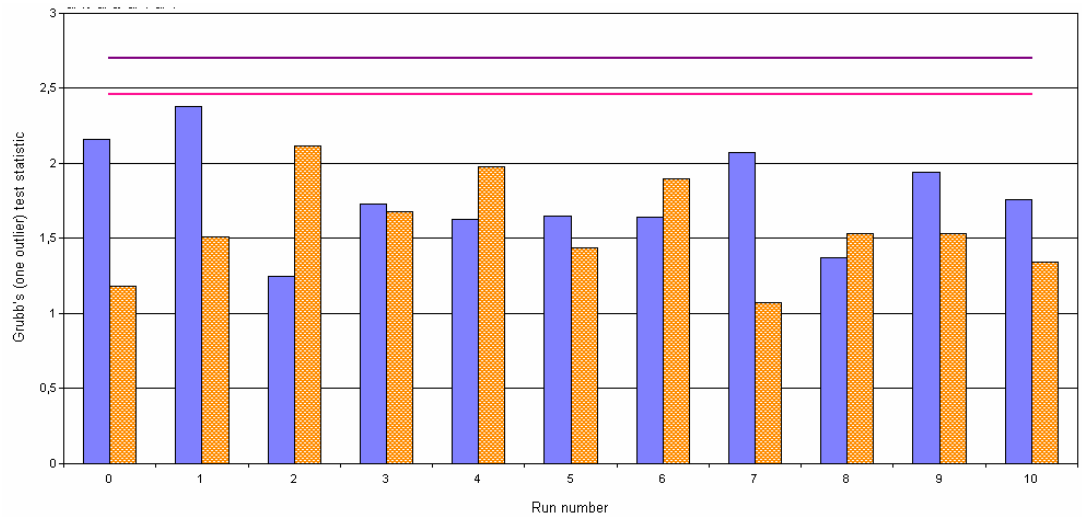

Figure 63: Grubb's one outlying observation test statistics for NO_2 runs.

Grubb's two outlying observations test statistics for the minimum (blue) and maximum (orange with pattern) values of all runs that passed "Grubb's one outlying observation" test. Values between the two lines are considered strugglers and values under red line are considered outliers.

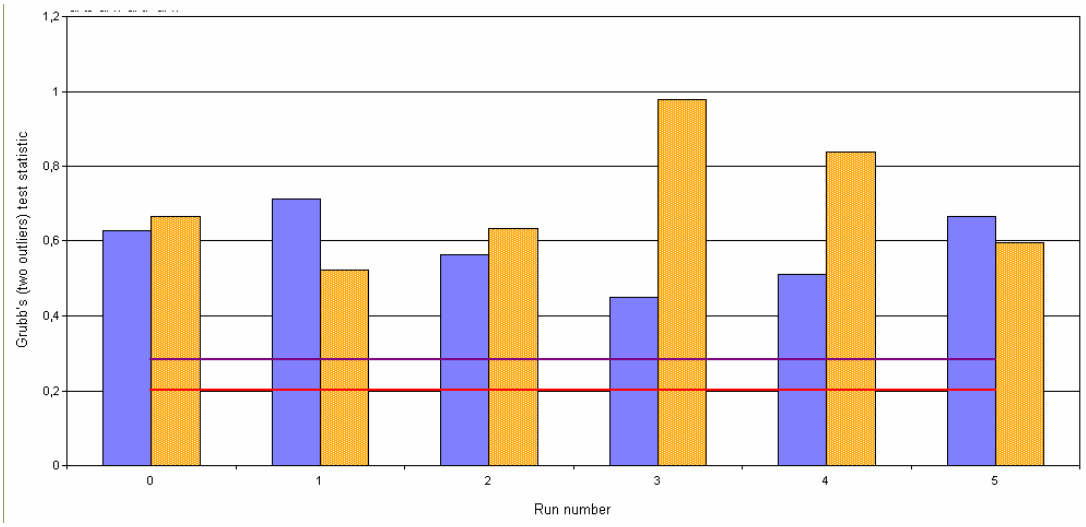

Figure 64: Grubb's two outlying observations test statistics for SO_2 runs

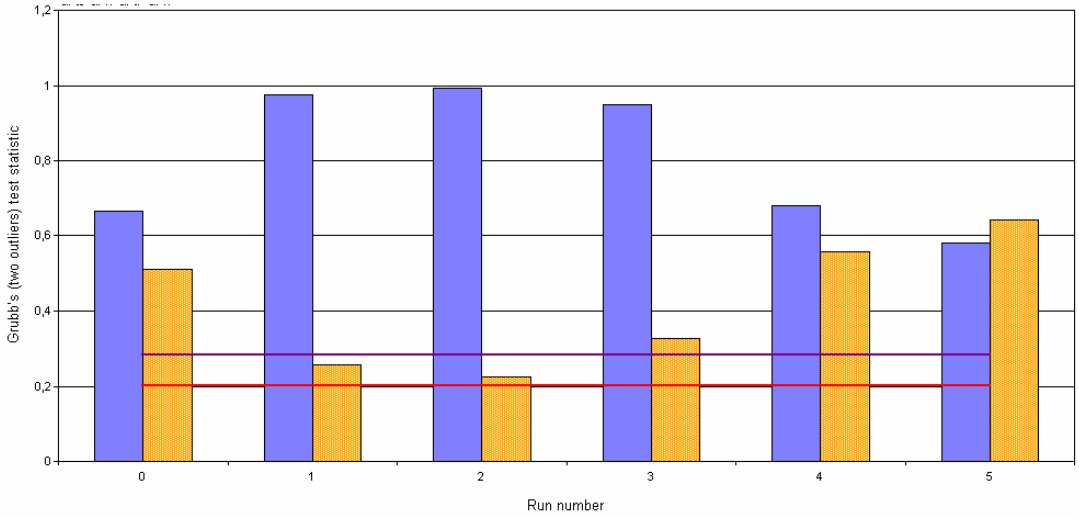

Figure 65: Grubb's two outlying observations test statistics for CO runs

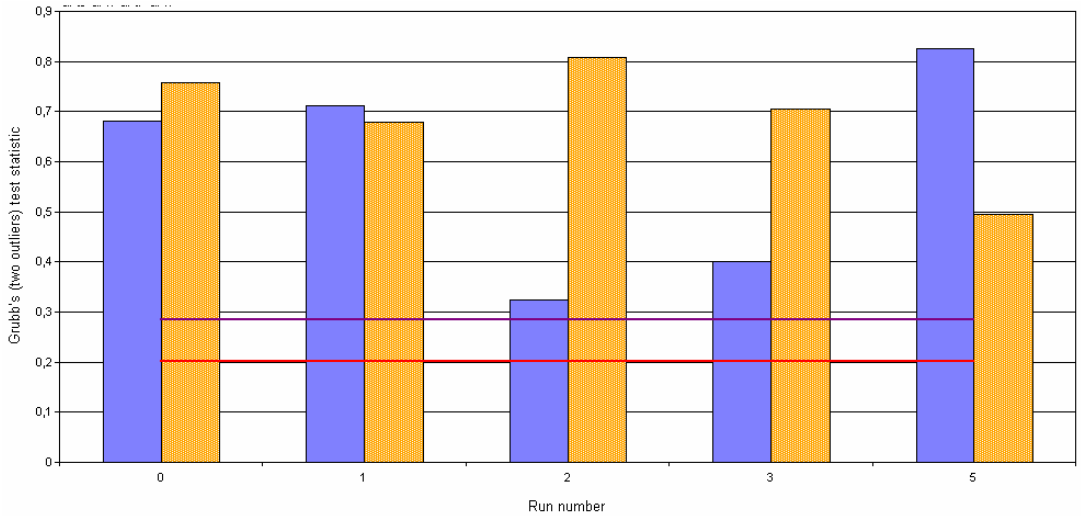

Figure 66: Grubb's two outlying observations test statistics for O3 runs

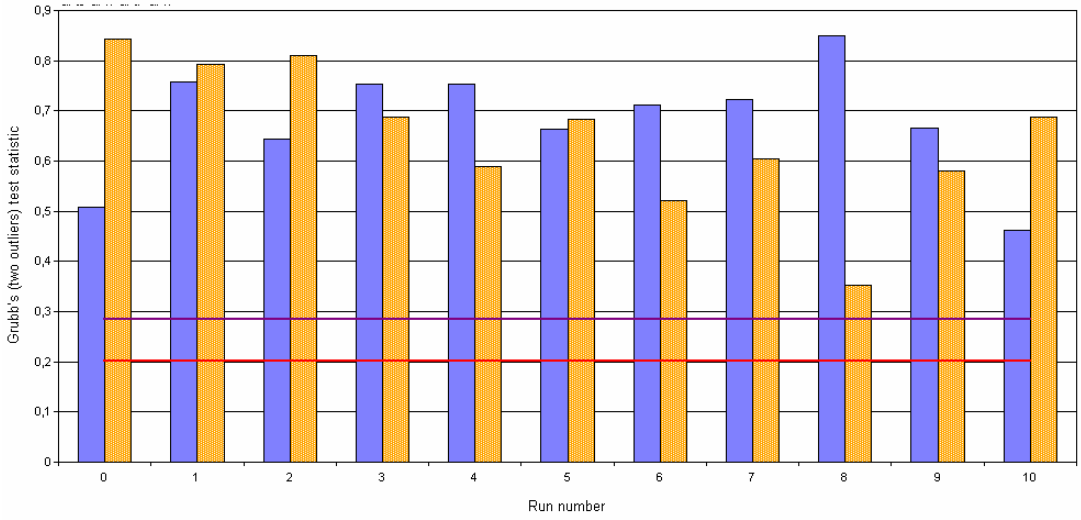

Figure 67: Grubb's two outlying observations test statistics for NO runs

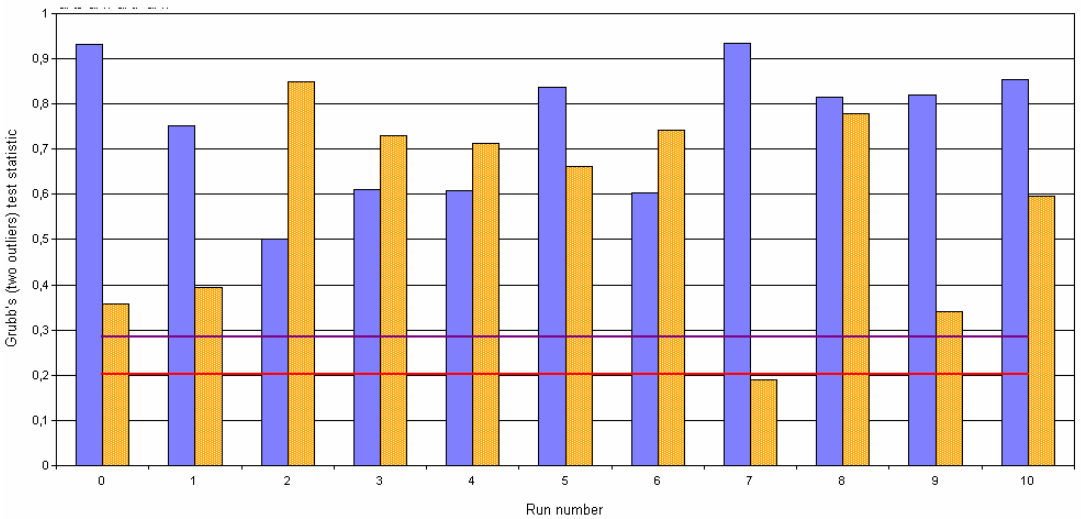

Figure 68: Grubb's two outlying observations test statistics for NO_2 runs

European Commission

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Abstract
In October 2007 in Essen (DE), 13 AQUILA and 5 WHO-EURO laboratories met at intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO2, CO, NO, NO2 and O3).

The proficiency evaluation, where each participant¿s bias was compared to two criteria, provides information on current situation to European Commission and can be used by participants in their QA/QC.

In terms of criteria imposed by European Commission, 65% of results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties while another 32% of results had good measured values but the reported uncertainties were either too small (5%) or too big (27%).

The comparability of results among AQUILA participants is satisfactory for O3, SO2, CO and NO measurement method but not for NO2 where further harmonization is needed.

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